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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/gsch20</u>

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Published online: 20 Jun 2012.

To cite this article: Yan Yang , Liu-Ting Yan , Wen-Gui Duan , Xiao Li & Rong-Huan Qin (2012) Synthesis, crystal structure and DNA interaction studies of three coordination polymers with mixed ligand, Supramolecular Chemistry, 24:10, 707-712, DOI: 10.1080/10610278.2012.695791

To link to this article: <u>http://dx.doi.org/10.1080/10610278.2012.695791</u>

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Synthesis, crystal structure and DNA interaction studies of three coordination polymers with mixed ligand

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(Received 18 December 2011; final version received 9 May 2012)

Three coordination polymers $[Mn(Nip)(Pbim)]_n$ (1), $[Co(Nip)(Pbim)]_n$ (2) and $[Zn(Nip)(Pbim)]_n$ (3) [5-nitroisophthalate (Nip) and 2-(2-pyridyl)benzimidazole (Pbim)] were synthesised and characterised by elemental analysis, IR and single-crystal X-ray diffraction. Single-crystal X-ray diffraction analysis reveals that 1, 2 and 3 have 1-D ladder chain structures constructed from μ_3 -bridge Nip ligands and metal atoms. All of these chain-like structures are finally packed into supramolecular networks through hydrogen bonds and $\pi - \pi$ stacking interactions. Fluorescence spectral method has been used for the study on the interaction of film sperm DNA with complexes. The results show that the corresponding fluorescence spectrum appeared and the intensity was enhanced with the growth of the concentration of DNA. All of the results indicate that there exists strong interaction of the complexes with DNA.

Keywords: crystal structure; mixed ligand; supramolecular network; fluorescence; DNA interaction

Introduction

The interaction of transition metal complexes with DNA has been extensively studied for their usage as probes for DNA structure and their potential application in molecular light switches, DNA footprinting agents, nucleic acid probes, chemotherapy and photodynamic therapy (1-3). One of the important DNA-related activity of the transition metal complexes is that some of the complexes show the ability to insert DNA (4). As the functional groups of the active sites of a number of enzymes, benzimidazole and its derivative can participate in many important biochemical reactions (5). So, the 2-(2-pyridyl)benzimidazole (Pbim) steps into our visions. In fact, as a chelate ligand Pbim has multiple coordination modes in forming metal coordination polymers. It can not only be chelate end blocking ligand but also be bridging ligand when it is deprotonated (6-8), which is different from the benzimidazole ligand (9). On the other hand, the containing N atoms derived from the ligand can act as hydrogen-bond acceptors or can play important roles in the construction of supermolecular structures. With the aim of extending the coordination chemistry based on mixed ligands, we add 5-nitroisophthalate (Nip) in the reactions. Nip is a versatile ligand in the synthesis of coordination polymers because its two carboxylic groups can bond with metal centres and the nitro group as an electron-withdrawing group coexisting in isophthalic acid, which can not only act as a hydrogen-bond acceptor, but also take on some spatial effects (10-18).

Herein, we report the synthesis, structural characterisations and photoluminescence properties of three coordination polymers constructed from Nip and Pbim. Significant intermolecular hydrogen bonding and $\pi - \pi$ stacking interactions extend the 1-D arrangement into the supramolecular framework. And, we mainly focused on exploring the trend in DNA-binding affinities of three complexes with mixed ligands and the spectroscopic properties of these complexes in response to pH changes.

Experimental

Materials and methods

Film sperm DNA (FS-DNA) was purchased from the Sino-American Biotechnology Company. Other reagents were bought from commercial sources and used without further purification. IR spectra were recorded in the range of 4000-400 cm⁻¹ on Perkin-Elmer Spectrum One FT/IR spectrometer using a KBr pellet. Elemental analysis (C, H, N) was carried out on a Perkin-Elemer 2400II CHN elemental analyzer. Emission spectra were measured on Ls55 spectrofluorophotometer. The crystal structure was determined by a Bruker APEX area-detector diffractometer and employing the SHELXTL crystallographic software. Buffer [5 mM tris(hydroxymethyl)aminomethane (Tris) hydrochloride, 50 mM NaCl, pH 7.5] was used for emission titration experiments. The concentration of FS-DNA was determined spectrophotometrically assuming a molar absorption of $6600 \,\mathrm{M^{-1} \, cm^{-1}}$

ISSN 1061-0278 print/ISSN 1029-0478 online © 2012 Taylor & Francis http://dx.doi.org/10.1080/10610278.2012.695791 http://www.tandfonline.com

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(260 nm) (19, 20). The emission titration of three complexes was carried out by using a fixed complex concentration to which increments of the DNA stock solution were added. The concentration of complexes solution was 10 μ M. Complex-DNA solutions were allowed to incubate for 15 min before the emission spectra were recorded. The pH dependence of the excited state properties of these complexes is investigated by fluorescence spectra. Fluorescence pH spectroscopic titrations of these complexes are carried out in dimethyl sulfoxide (DMSO)–Tris buffer (1:1) solution with 0.2 M NaCl to maintain a constant ionic strength. All spectral changes with pH are reversible.

Synthesis of $[Mn(Nip)(Pbim)]_n$ (1)

For the hydrothermal reaction of MnCl₂·4H₂O (0.5 mmol), Hpbim (0.25 mmol), H₂nip (0.25 mmol) and water (15 ml), the mixture was stirred for 10 min in air, then transferred and sealed into a 23 ml Teflon reactor, which was heated at 100°C for 2 days and then cooled to room temperature. Colourless crystals were obtained (yield 52% based on Mn), filtered off, washed with distilled water and dried in air. Elemental analysis (%): Anal. Calcd C 52.30, H 2.63, N 12.20; found C 51.96, H 2.91, N 11.87. IR (KBr pellets, cm⁻¹): $\nu = 3445$, 3089, 1626, 1609, 1569, 1539, 1451, 1421, 1377, 1365, 1347, 1322, 1149, 1075, 976, 792, 747, 548.

Synthesis of $[Co(Nip)(Pbim)]_n$ (2)

Complex **2** was obtained by a similar procedure described as complex **1**. For the hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), Hpbim (0.25 mmol), H_2nip (0.25 mmol) and water (15 ml), the mixture was stirred for 20 min in air, then transferred and sealed into a 23 ml Teflon reactor, which was heated at 110°C for 4 days and then cooled to room temperature. Red needle-shaped crystals were obtained (yield 48% based on Co), filtered off, washed with distilled water and dried in air. Elemental analysis (%): Anal. Calcd C 51.14, H 2.57, N 11.93; found C 50.72, H 2.89, N 11.81. IR (KBr pellets, cm⁻¹): $\nu = 3434$, 3082, 1626, 1608, 1566, 1541, 1454, 1421, 1379, 1360, 1347, 1300, 1157, 1075, 984, 781, 747, 554.

Synthesis of $[Zn(Nip)(Pbim)]_n$ (3)

Complex **3** was also obtained by a similar procedure described as complex **1**. For the hydrothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), Hpbim (0.25 mmol), H_2nip (0.25 mmol) and water (15 ml), the mixture was stirred for 30 min in air, then transferred and sealed into a 23 ml Teflon reactor, which was heated at 120°C for 3 days and then cooled to room temperature. Colourless crystals were obtained (yield 42% based on Zn), filtered off, washed

with distilled water and dried in air. Elemental analysis (%): Anal. Calcd C 47.92, H 3.62, N 11.18; found C 47.59, H 4.01, N 10.81. IR (KBr pellets, cm⁻¹): $\nu = 3434$, 3082, 1629, 1611, 1572, 1542, 1455, 1421, 1380, 1358, 1347, 1303, 1152, 1075, 982, 784, 747, 551.

X-ray crystallography

The diffraction data were collected on a Bruker Smart Apex CZN diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 296 K. Absorption correction was applied by SADABS (21). The structure was solved by Direct Methods and refined with full-matrix least-squares technique using SHELXTL (22). All nonhydrogen atoms were refined with anisotropic displacement parameters. The crystal data, details on the data collection and refinement are summarised in Table 1, and selected bond lengths and angles are presented in Table 2; the hydrogen bond lengths (Å) and bond angles (deg) are listed in Table 3.

Crystal structures of complexes 1, 2 and 3

Single-crystal X-ray diffraction analysis reveals that compounds 2 and 3 are isostructural and crystallise in the monoclinic C2/c space group. Only structure 2 is described here in detail. Compound 2 has a supramolecular framework structure formed by 1-D ladder chains. Asymmetric unit contains one Co atom, one Pbim ligand and one Nip ligand (Figure 1(a)). Each Co atom is coordinated to two N atoms from one Pbim ligand and three O atoms from three Nip ligands, and adopts a distorted square-pyramidal coordination environment. The Co-O distances are in the range of 1.968(3) - 2.055(3) Å, and the Co-N distances are in the range of 2.052(3)-2.136(3) Å, respectively. In the structure, the Nip ligand adopts μ_3 -bridge coordination fashion: one carboxylate group adopts bis-monodentate coordination mode to bridge two Co(II) centres, and another carboxylate group acts as a monodentate ligand. The adjacent Co(II) is connected by μ_3 -bridged Nip into 1-D ladder chain (Figure 1(b)). It should be noted that the uncoordinated O atoms of Nip ligand act as hydrogen-bonding acceptors to form hydrogen bonds with N of Pbim ligands, in which O...N separations of 3.350(5) Å, and O-H...N angles of 154.00° (Figure 2(a)). And Pbim ligand still acts as a chelating ligand and alternately decorated at both sides of the chains. The 1-D chains mentioned above are interconnected through these hydrogen bonds and $\pi - \pi$ stacking interactions between the adjacent Pbim groups (the distance is 3.578(2)Å) to result in a layer structure (Figure 2(b)) and further stabilise the supramolecular network. The structure of **1** is very similar to complexes **2** and 3, which may be attributed to the influence of different coordination geometries of metal ions (6).

Identification code	1	2	3
Empirical formula	$C_{20}H_{12}MnN_4O_6$	$C_{20}H_{12}CoN_4O_6$	$C_{20}H_{12}ZnN_4O_6$
Formula weight	459.28	463.27	469.37
Temp (K)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
<i>a</i> (Å)	20.336(7)	20.073(17)	20.167(7)
b (Å)	14.315(5)	14.070(11)	14.008(3)
<i>c</i> (Å)	19.477(6)	13.944(12)	13.909(3)
β (°)	138.12(2)	113.034(11)	113.86(2)
$V(\text{\AA}^3)$	3785(3)	3624(5)	3593.5(17)
Cryst size (mm)	$0.18 \times 0.20 \times 0.22$	$0.26 \times 0.26 \times 0.28$	$0.16 \times 0.16 \times 0.18$
Ζ	8	8	8
$D_c (\mathrm{g cm}^{-3})$	1.612	1.698	1.499
$\perp (mm^{-1})$	0.746	0.998	0.905
F (000)	1864	1880	1643
Limiting indices	$-21 \le h \le 24$	$-18 \le h \le 23$	$-22 \le h \le 23$
	$-17 \le k \le 17$	$-15 \le k \le 16$	$-16 \le k \le 16$
	$-23 \le l \le 11$	$-15 \le l \le 16$	$-15 \le l \le 16$
Reflections	9894	9536	9430
Independent	3337	3194	3160
Observed data	2541	2443	877
Npar	280	280	126
R _{int}	0.096	0.041	0.238
GOF	1.83	1.03	0.85
$R_1^{a} (I > 2\sigma(I))$	0.0605	0.0375	0.1477
wR_2^{b} (all data)	0.0905	0.1006	0.4040
Max/min electron density (e \AA^{-3})	0.56/-0.55	0.38/-0.41	2.34/-3.51
Theta range (°)	1.8, 25.0	1.8, 25.0	1.8, 25.0

Table 1. Crystal data and structure refinement for 1-3.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$ ${}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$

Table 2. Selected bond lengths (Å) and bond angles (°) for complexes 1-3.

Complex 1		Comple	Complex 2		Complex 3	
Mn1-O1	2.038(3)	Co1-O1	2.031(3)	Zn1-O1	2.003(12)	
Mn1-N1	2.264(3)	Co1-O2	2.055(3)	Zn1-N1	2.155(15)	
Mn1-N2	2.207(3)	Co1-O3	1.968(3)	Zn1-N2	2.066(14)	
Mn1-O8b	2.095(3)	Co1-N1	2.136(3)	Zn1-O2a	2.082(13)	
Mn1-O7d	2.159(4)	Co1-N2	2.052(3)	Zn1—O6b	1.916(13)	
O1-Mn1-N1	100.16(11)	O1-Co1-O2	87.28(9)	O1–Zn1–N1	162.3(5)	
O1-Mn1-N2	114.61(13)	O1-Co1-O3	95.92(9)	O1–Zn1–N2	97.7(5)	
O1-Mn1-O8b	101.77(12)	O1-Co1-N1	168.52(9)	O1–Zn1–O2a	87.2(5)	
O1-Mn1-O7d	99.22(13)	O1-Co1-N2	97.91(9)	O1–Zn1–O6b	96.8(5)	
N1-Mn1-N2	74.13(14)	O2-Co1-O3	100.68(9)	N1-Zn1-N2	76.7(6)	
O8b-Mn1-N1	158.08(11)	O2-Co1-N1	89.79(9)	O2a-Zn1-N1	88.1(6)	
O7d-Mn1-N1	88.76(14)	O2-Co1-N2	143.74(9)	O6b-Zn1-N1	100.8(5)	
O8b-Mn1-N2	96.47(12)	O3-Co1-N1	95.53(9)	O2a-Zn1-N2	144.3(5)	
O7d-Mn1-N2	144.03(13)	O3-Co1-N2	114.30(9)	O6b-Zn1-N2	116.8(6)	
O7d-Mn1-O8b	87.84(14)	N1-Co1-N2	78.07(9)	O2a-Zn1-O6b	97.5(5)	

Symmetry transformations used to generate equivalent atoms: Complex 1, b = 1/2 - x, -1/2 - y, 1 - z; d = 1/2 + x, -1/2 - y, 1/2 + z. Complex 3, a = -x, y, 1/2 - z; b = -x, 1 - y, -z.

IR spectra

For the coordination modes of carboxylate group, the difference between the asymmetric (ν_{as}) and symmetric (ν_{s}) carboxylate stretches ($\Delta = \nu_{as} - \nu_{s}$) is often used (23). The IR spectra of 1-3 are similar (Figure S1 of the Supplementary Information, available online). As representative, only the IR and Raman spectra of 2 are described here in details. The strong and broad absorption at 3445 cm^{-1} suggests the presence of N–H stretch vibrations. Compared with the free H₂nip, the disappearance of band at

		6 1		
D—H…A	<i>d</i> (D—H)	$d(H \cdots A)$	d(D - A)	<(D—H…A)
Complex 1				
02-H17-N1	0.8200	2.6000	3.350(5)	154.00
C47—H47…O6	0.9300	2.4300	3.078(4)	127.00 (1/2 + x, 1/2 - y, 1/2 + z)
Complex 2				
N3-H3-04	0.8600	1.8700	2.707(4)	165.00 (x, 1 + y, z)
С3—Н3А…О5	0.9300	2.4800	3.116(4)	126.00 (2 - x, 1 + y, 1/2 - z)
Complex 3				
N3-H3-05	0.8600	1.9000	2.75(2)	164.00 (x, -1 + y, z)
C4—H4…O4	0.9300	2.3700	3.04(3)	129.00 (-x, -1 + y, 1/2 - z)

Table 3. Distances (Å) and angles (°) of hydrogen bonds for complexes 1-3.



Figure 1. (a) Coordination environment of complex 2 and (b) 1-D chain of complex 2, hydrogen atoms are omitted for clarity.



Figure 2. (a) $\pi - \pi$ Stacking and hydrogen-bonding interactions and (b) 2-D layers along *ab* plane.

1718 cm⁻¹ in **2** is indicative of the full deprotonation of aromatic acid. The characteristic absorptions for the asymmetric and symmetric vibrations of the carboxylate of the ligand are observed at 1626, 1569, 1451 and 1347 cm⁻¹, respectively. And their difference ($\Delta v = v_{as} - v_s = 175$ and 222 cm⁻¹) suggests the coexistence of the biand monodentate modes of Nip anion (23). These conclusions are also supported from the results obtained from X-ray diffraction measurements. The weak bands observed in the 450–554 cm⁻¹ region are due to Co–O and Co–N stretching vibrations (24).

Raman spectra

Raman spectrum of complex **2** in the frequency region $(100-2000 \text{ cm}^{-1})$ is shown in Figure 3. The relative strong bands are observed when excited with the line at 514 nm. The peaks with frequency lower than 300 cm⁻¹ may be the vibration of Co^{II}, which is relatively weak as observed in Raman spectrum. The peak at 570 and 709 cm⁻¹ may be the wagging and rocking modes of the coordinate nitrogen atoms, respectively (23, 24). The COO⁻ symmetric and asymmetric stretching mode at 1434 and 1525 cm⁻¹, respectively, and 1564 cm⁻¹ is assigned to C = O



Figure 3. Raman spectrum of complex 2 at room temperature.

stretching. Both the 1015 cm^{-1} band (C-COO⁻ stretching motions) and the 1618 cm^{-1} band (C-C stretching) are relatively strong in Raman spectrum (23, 24).

DNA interaction studies

Upon excitation using a wavelength of 310 nm for complexes, all of the complexes can emit fluorescence with a maximum wavelength of about 370 nm. The results of the emission titration for these complexes with DNA are shown in Figures 4–6. The fluorescence intensity of these complexes increased with the increase in DNA concentration, reaching a maximum at the ratio of [Complex]/[DNA] = 0.4, at which there is a 3.26, 2.89 and 3.07-fold increase in the fluorescence intensity of the complexes compared with that in the absence of DNA for 1, 2 and 3, respectively. This indicates that complexes bind with DNA by intercalation, and such enhancement could be ascribed to the fact that the intercalation of the complex into DNA, which is hydrophobic inside the helix, limits the



Figure 4. Fluorescence emission spectra of the FS-DNA in 0.1 M tris buffer (pH = 7.5) containing 10% DMSO in presence of complex 1. $\lambda_{ex} = 310$ nm.



Figure 5. Fluorescence emission spectra of the FS-DNA in 0.1 M tris buffer (pH = 7.5) containing 10% DMSO in presence of complex 2. $\lambda_{ex} = 310$ nm.



Figure 6. Fluorescence emission spectra of the FS-DNA in 0.1 M tris buffer (pH = 7.5) containing 10% DMSO in presence of complex 3. $\lambda_{ex} = 310$ nm.

collision and energy dissipation with the environmental water and oxygen (25-27).

Effect of pH value

The pH-dependent emission spectra of complexes upon stepwise addition of NaOH in CH_3OH are shown in Figure 7, Figures S2 and S3 of the Supplementary Information, available online. Addition of NaOH to DMSO solution of complex 1 caused the weak emission maximum at 372 nm. The same method was used and, addition of NaOH solution to DMSO solution of complexes 2 and 3 still caused the weak emission at 368 and 371 nm, respectively. At pH 5.7, all complexes exhibit the highest intensity of emissions. It can come to the conclusion that the intensity of emissions in acid solution is higher than that in base solution. The emission energy is



Figure 7. Emission spectra of complex 1 at a concentration of 2×10^{-5} M upon stepwise addition of NaOH in CH₃OH with 0 (pH = 1.1), 0.1 (2.4), 0.4 (5.7), 0.6 (6.7), 0.8 (7.6), 1 (8.6), 14 (10.1) and 24 (11.4) equiv of NaOH added. $\lambda_{ex} = 310$ nm.

ascribed to the conjugation effect of the organic ligand Pbim (28-30).

Summary

In conclusion, we successfully synthesised three novel coordination polymers based on Pbim and Nip ligands with different metals by solvothermal method. All these compounds get the supramolecular structures through intermolecular interactions. It demonstrates that the weakly intermolecular interactions, such as hydrogen bonding, $\pi \cdots \pi$ stacking interactions and C—H…O stacking interactions, play a very important role in controlling the coordination polymers, especially further linking the 1-D entities into supramolecular networks. DNA interaction studies were investigated by fluorescence spectral method, and we observed a similarity in DNA binding by three coordination polymers and the spectroscopic properties in response to pH changes.

Supplementary materials

CCDC Nos 827560 (1), 840879 (2) and 840880 (3), contain the supplementary crystallographic data. These data can be obtained via the Cambridge Crystallographic Data Centre (deposit@ccdc.cam.ac.uk; http://www.ccdc. cam.ac.uk/deposit).

Acknowledgements

We acknowledge financial support by the National Natural Science Foundation of China (No. 51062016) and the Natural Science Foundation of the Education Committee of Guangxi Province (No. 200911MS199).

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