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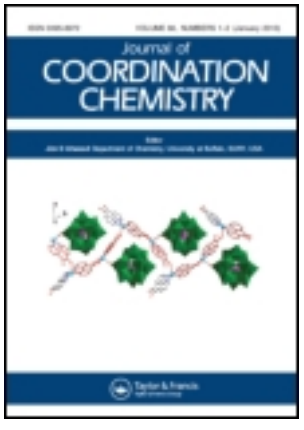

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A new N,N-bis(2-pyridylmethyl)methylamine iron(III) complex: synthesis, structure, DNA binding, and nuclease activity

Jing Qian [a], Liping Wang [b], Jinlei Tian [c] & Shiping Yan [c]

[a] College of Chemistry, Tianjin Normal University, Tianjin 300387, P.R. China

[b] Department of Chemistry, Baoding College, Baoding 071000, P.R. China

[c] College of Chemistry, Nankai University, Tianjin 300071, P.R. China

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A new *N,N*-bis(2-pyridylmethyl)methylamine iron(III) complex: synthesis, structure, DNA binding, and nuclease activity

JING QIAN*†, LIPING WANG‡, JINLEI TIAN§ and SHIPING YAN§

†College of Chemistry, Tianjin Normal University, Tianjin 300387, P.R. China
‡Department of Chemistry, Baoding College, Baoding 071000, P.R. China
§College of Chemistry, Nankai University, Tianjin 300071, P.R. China

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A new iron(III) complex, [Fe(bpma)Cl_3] (**1**) (bpma = *N,N*-bis(2-pyridylmethyl)methylamine), has been synthesized and determined by X-ray diffraction. Complex **1** crystallizes in the orthorhombic space group P_{nma}, with FeN_3Cl_3 core, average *d*(Fe–N) of 2.212 Å, and average *d*(Fe–Cl) of 2.293 Å. Elemental analysis and infrared spectra of the complex were also determined. Complex **1** is soluble in water and organic solvents, facilitating investigation of its behavior in solution. Interaction with calf thymus-DNA (ct-DNA) for **1** investigated by UV absorption and fluorescence spectroscopy shows **1** binds to ct-DNA with moderate intercalation. The interaction between **1** and pBR322 DNA has also been investigated by submarine gel electrophoresis; the complex exhibits effective DNA cleavage activity in the absence of activating agents under similar physiological conditions.

Keywords: Iron(III); Crystal structure; DNA binding; DNA cleavage

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1. Introduction

The ligands bpa-R, first reported by Romary *et al*. [1], are classical tridentate nitrogen donors which can bind to metals both facial and meridional [2], and are more flexible than triazacyclononane (TACN), which is strictly facially coordinating [3–5]. Like trispyrazolylborates, bpa-R can adopt both k_2 and k_3 coordination, but unlike trispyrazolylborates it can coordinate in facial and meridional k_3 modes [6]. A variety of transition metal complexes with bpa-R have been reported [7–17]. Previously, we reported several complexes with bpa-R [18–24]. But studies on Fe complexes with bpa-R ligands are limited [23, 24]. Herein, we report the synthesis, crystal structure, and spectroscopic properties of a new iron(III) complex with bpma (bpma = *N,N*-bis(2-pyridylmethyl)methylamine), [Fe(bpma)Cl_3] (**1**). The rare-cutting restriction endonuclease *Not*I contains a unique iron-binding fold that positions nearby protein elements for DNA recognition and serves as a structural role [25]. A detailed investigation into the DNA binding and DNA cleavage activities of **1** is also presented.

*Corresponding author. Email: qianjinger@yahoo.com.cn

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2. Experimental

2.1. *Materials*

All analytical reagents were obtained from commercial sources and used without purification. Solvents used in this research were purified by standard procedures. Bpma was prepared following a literature method [26]. Unless otherwise stated, all reagents used in this research were obtained from Sigma Chemical Co. Tris-HCl buffer solution was prepared by using deionized, sonicated triply-distilled water (Tris is tris-hydroxymethyl-aminomethane).

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2.2. *Measurements*

C, H, and N elemental analyses were obtained on a Perkin-Elmer analyzer model 240. Infrared (IR) spectroscopy as KBr pellets was performed on a Bruker Vector 22 FT-IR spectrophotometer from 4000 to 400 cm^{-1}. The electronic spectrum was measured on a JASCO V-570 spectrophotometer. The fluorescence spectrum was recorded on a Cary 300 fluorescence spectrophotometer. The Gel Imaging and documentation DigiDoc-It System were assessed using Labworks Imaging and Analysis Software (UVI, England).

2.3. *Preparation of [Fe(bpma)Cl_3] (1)*

To an acetonitrile solution (5 mL) of $FeCl_3$ (0.162 g, 1.0 mmol) was added dropwise an acetonitrile solution (15 mL) of bpma (1.0 mmol) with stirring. The yellow powder obtained by evaporation of this solution at room temperature was washed with diethyl ether and dried in air. The powder (1.0 mmol) was redissolved in a mixture of DMSO/CH_3OH/DMF (0.5 : 2 : 1). Two weeks later, yellow block crystals were obtained by slow evaporation of this solution at room temperature (yield: 121 mg, 32%). Anal. Calcd for $C_{13}H_{15}Cl_3FeN_3$ (375.48) (%): C, 41.58; H, 4.03; N, 11.19. Found (%): C, 41.79; H, 4.34; N, 10.87.

2.4. *Crystallographic data collection and structure determination*

Single crystals of **1** were put on a Bruker Smart 1000 CCD diffractometer, equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected at room temperature by the φ–ω scan mode. The details of crystallographic data and structure refinement parameters are summarized in table 1. The structure was solved by direct methods and refined with full-matrix least-squares using SHELXS-97 and SHELXL-97 [27, 28]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Organic hydrogens were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated.

2.5. *DNA binding and cleavage experiments*

DNA-binding experiments were performed at room temperature. Solution of calf thymus-DNA (ct-DNA) gave a ratio of UV absorbance at 260 and 280 nm, A_{260}/A_{280},

Table 1. Crystallographic data and structure refinement parameters for **1**.

Complex	**1**
Empirical formula	$C_{13}H_{15}Cl_3FeN_3$
Formula weight	375.48
Crystal system	Orthorhombic
Space group	P_{nma}
Unit cell dimensions (Å)	
a	14.220(18)
b	14.604(19)
c	7.495(10)
Volume (Å^3), Z	1556.5(4), 4
Calculated density (Mg m^{-3})	1.602
Absorption coefficient (mm^{-1})	1.476
F(000)	764
Crystal size (mm^3)	$0.28 \times 0.22 \times 0.20$
θ range for data collection	2.79–25.03
Limiting indices (h, k, l)	−16 to 16, −16 to 17, −7 to 8
Reflections collected	7946
Independent reflections	1428 [$R_{int} = 0.0261$]
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	1428/0/97
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0242$, $wR_2 = 0.0605$
R indices (all data)	$R_1 = 0.0307$, $wR_2 = 0.0633$
Largest difference peak and hole (e Å^{-3})	0.193 and −0.227

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of 1.86, indicating that the DNA was sufficiently free of protein [29]. The ct-DNA stock solutions were prepared in 5 mmol L^{-1} Tris-HCl/NaCl buffer, pH = 6.0 (stored at 4°C and used within 4 days after their preparation). The concentration of ct-DNA was determined from its absorption intensity at 260 nm with a molar extinction coefficient of 6600 (mol L^{-1})$^{-1}$ cm^{-1} [30].

UV-Vis absorption spectroscopy experiments were conducted by adding ct-DNA solution to **1** (23.9 μmol L^{-1}) at different concentrations (0–159 μmol L^{-1}). By the fluorescence spectral method, the relative binding of **1** to ct-DNA was studied with an ethidium bromide (EB)-bound ct-DNA solution. The excitation wavelength was fixed at 510 nm and the emission range was adjusted before measurements. Fluorescence intensities at 602 nm were measured at different complex concentrations [31].

Cleavage of supercoiled pBR322 DNA by the complex was studied by agarose gel electrophoresis. The reaction was carried out following a literature method [32]. Bands were visualized by UV light and photographed. The resolved bands were visualized by ethidium bromide staining and were then quantified. A correction factor of 1.22 was utilized to account for the decreased ability of EB to intercalate into Form I DNA compared with Form II [33].

3. Results and discussion

3.1. *Crystal structure of 1*

Complex **1** shows good solubility in water, high solubility in methanol, ethanol, DMF, DMSO, and CH_3CN. The complex has been structurally characterized by single-crystal

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

Fe(1)–N(1)	2.198(16)	Fe(1)–Cl(1)	2.306(6)
Fe(1)–N(2)	2.240(2)	Fe(1)–Cl(2)	2.266(9)
N(1)–Fe(1)–N(1A)	75.98(8)	N(1)–Fe(1)–Cl(2)	93.46(5)
N(1)–Fe(1)–N(2)	77.11(6)	N(1A)–Fe(1)–Cl(2)	93.46(5)
N(1)–Fe(1)–Cl(1)	90.28(4)	N(2)–Fe(1)–Cl(2)	167.95(6)
N(1A)–Fe(1)–Cl(1)	163.02(5)	N(2)–Fe(1)–Cl(1)	90.26(4)
Cl(2)–Fe(1)–Cl(1)	97.35(2)	Cl(1)–Fe(1)–Cl(1A)	101.22(3)

Symmetry transformations used to generate equivalent atoms: A: x, $-y+3/2$, z.

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X-ray crystallography. Selected bond lengths and angles are listed in table 2. The complex crystallizes as [Fe(bpma)Cl_3] in the orthorhombic system, P_{nma} space group, $Z=4$. The labeling diagram of the neutral molecule is shown in figure 1. Complex **1** possess a mirror plane of symmetry, which contains Cl(2), Fe(1), N(2), and C(7). In **1**, Fe is a distorted octahedron with N_3Cl_3 donor sets derived from three nitrogens of bpma and three chlorides, with the basal plane formed by N(1), N(1A), Cl(1), Cl(1A) and the axial positions occupied by N(2) and Cl(2). The average Fe–N bond length is 2.212 Å and average Fe–Cl bond average length is 2.293 Å.

3.2. *IR spectrum studies*

For **1**, $\nu_{(C-N)}$ is indicated by a shoulder involving a split sharp peak at 1600 cm^{-1}, while $\nu_{(C-H)}$ is a split sharp peak at 3042, 3017, and 2908 cm^{-1}. Abundant absorptions in the region 620 ~ 770 cm^{-1} strongly argue for the presence of pyridyls.

3.3. *DNA-binding properties*

The binding ability of **1** to ct-DNA was studied by various techniques. Binding ability of **1** to ct-DNA was studied by UV spectroscopy by following the intensity changes of the intraligand π–π^* and π–n transitions, as shown in figure 2. Absorptions at 209 and 258 nm are attributed to intraligand π–π^* and π–n transitions, respectively. Increasing the concentration of ct-DNA, hypochromisms of 39%–17% and red-shifts of 13–2 nm were observed. Although this is not definitive proof, hypochromism and red shifts for other complexes in the presence of ct-DNA are often taken as a sign of an intercalative binding mode, where stacking interactions between the aromatic chromophore of the complex and the base pairs of DNA modulate the absorption characteristics of the metal complexes [34]. The value of the intrinsic binding constant (K_b) was determined to be 3.97×10^4 for **1** by regression analysis [35]. The value is ~100 times lower than those reported for classical intercalators (e.g. EB-DNA, $\sim 10^6$ $(mol\,L^{-1})^{-1}$) [36] and about an order of magnitude lower than those of intercalators containing similar planar ligands [37]. The extent of the hypochromism is commonly consistent with the strength of intercalative interaction. The lower K_b observed for **1** implies that it does not intercalate very strongly or deeply between the DNA base pairs. So we propose that the lower red shifts observed in the UV spectra are due to the partial/moderate intercalation of pyridyl ligand.

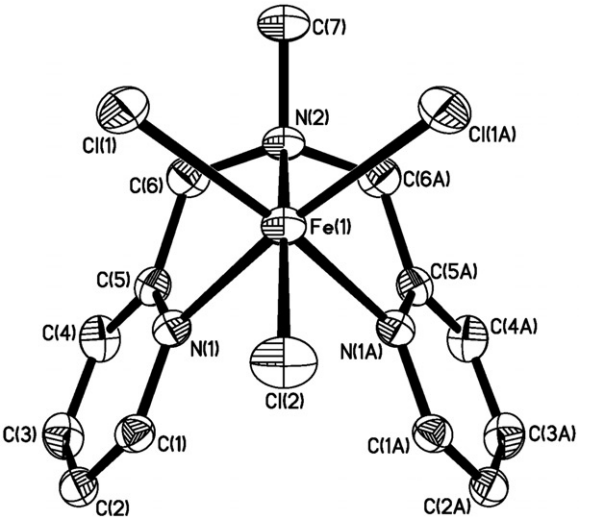

Figure 1. The labeling scheme of [Fe(bpma)Cl_3]. Hydrogens are omitted for clarity.

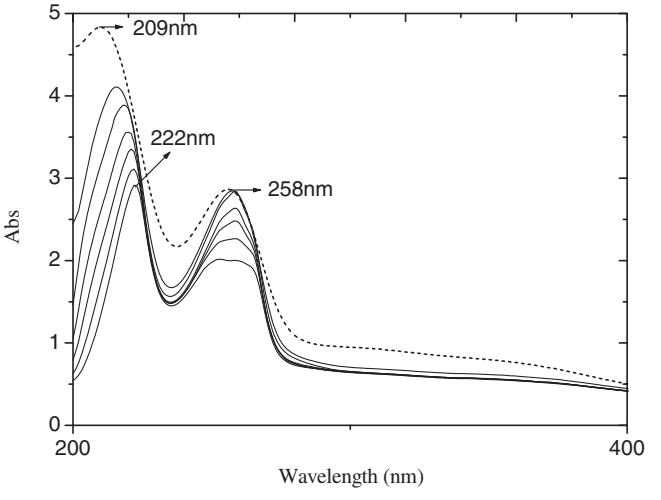

Figure 2. Absorption spectra of **1** (2.39×10^{-5} mol L^{-1}) in the absence (dashed line) and presence (solid line) of increasing amounts of ct-DNA (0–1.59×10^{-4} mol L^{-1}) at room temperature in 5 mmol L^{-1} Tris-HCl/NaCl buffer (pH = 6.0).

To further clarify the binding of **1**, fluorescence spectral measurement was carried out. EB does not show any appreciable emission in buffer solution due to fluorescence quenching of the free EB by solvent [38]. EB emits intense fluorescence at 600 nm in the presence of DNA due to its strong intercalation between adjacent DNA base pairs [39]. Enhanced fluorescence could be quenched by the addition of another molecule [40]. No luminescence was observed for **1** at room temperature in aqueous solution or in the presence of ct-DNA, so the binding of **1** cannot be directly presented in the

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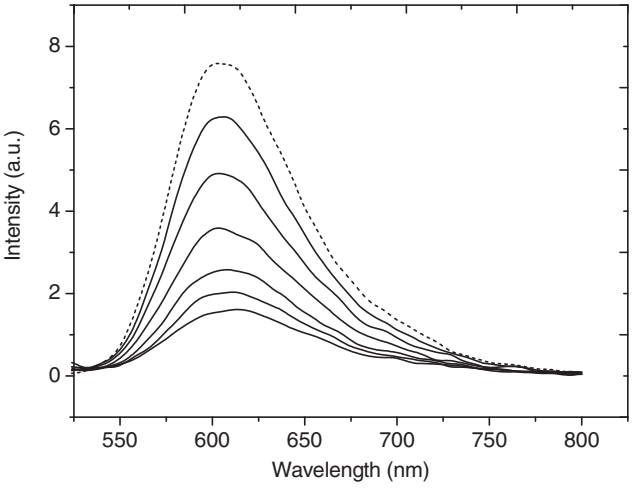

Figure 3. Emission spectra of EB-ct-DNA in the absence (dashed line) and presence (solid lines) of **1** at 293 K.

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emission spectra. The relative binding of **1** to ct-DNA was studied with an EB bound ct-DNA solution in Tris-HCl buffer (pH = 6.0). Fluorescence intensities at 602 nm (526 nm excitation) were measured at different complex concentrations. Figure 3 showed that the fluorescence intensity of EB bound ct-DNA decreased with the addition of **1**, which indicated that **1** could bind to ct-DNA and replace EB from the EB-bound ct-DNA system. Such a feature is often found in intercalative DNA interactions [41].

3.4. *DNA cleavage activity*

The ability of **1** to cleave DNA was assayed with the aid of gel electrophoresis on supercoiled pBR322 plasmid DNA as a substrate in 50 mmol L^{-1} Tris-HCl/18 mmol L^{-1} NaCl buffer (pH 6.0) in the absence of external agent. When circular plasmid DNA is submitted to electrophoresis, the fastest migration will be observed for the supercoiled form (Form I). If one strand is cleaved, the supercoiled DNA will relax to produce a slower-moving nicked circular form (Form II). If both strands are cleaved, a linear form (Form III) will be generated which migrates between Form I and Form II.

The time-dependent cleavage of DNA by **1** was studied. With the increase in reaction time, the amounts of Form II increased and Form I gradually disappeared. When the time was 8 h (line 6), Form II disappeared and may partly turn into small fragments. The results show that cleavage of DNA by the complex is dependent on reaction time (figure 4). From these experimental results, we find that plots for the appearance of Form II as well as the disappearance of Form I follow pseudo-first-order kinetic profiles and fit well to a single-exponential decay curve, consistent with the general model for enzyme catalyzed reactions [42]. Fitting the experimental data with first-order consecutive kinetic equations, the rate constants, $k_{obs} = 7.1 \pm 0.3 \times 10^{-5}\,s^{-1}$ for **1**. Expectedly, the catalytic efficiency of **1** is about ~17 times lower than our previously

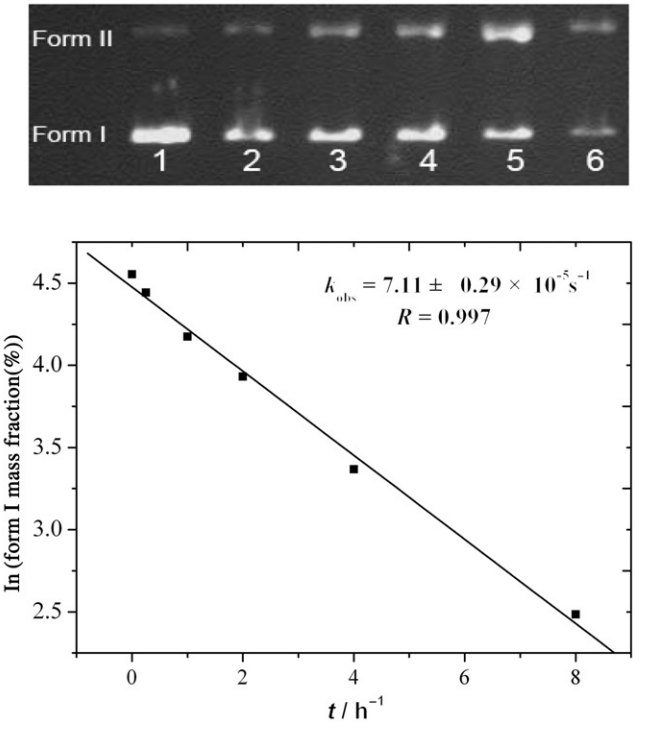

Figure 4. Time course of pBR322 DNA cleavage by **1** at pH 6.0 and 37°C: Lane 1, DNA control (2 h); Lane 2–6: DNA + 0.15 mmol L^{-1} **1** (0.25 h; 1 h; 2 h; 4 h; 8 h).

reported binuclear ferric complex [23]. The result shows that the reaction mechanism is really cooperative and cooperativity between the two ferric centers has been clearly demonstrated.

4. Conclusion

A new ferric complex has been synthesized and characterized both crystallographically and spectroscopically. The interaction of **1** with ct-DNA has been studied using UV absorption and fluorescence spectroscopy, and the mode of ct-DNA binding has been proposed. Complex **1** can effectively promote cleavage of plasmid DNA without addition of external agents at pH = 6.0 and 37°C. Based on the kinetics experiments, **1** shows catalytic activity. Unfortunately, such reactivity is counterbalanced by a moderate affinity for the substrate ($K_b \sim 10^4$ (mol L^{-1})$^{-1}$) so that long times (h) and higher concentration (0.15 mmol L^{-1}) is required to obtain a fast degradation of DNA. The synthesis of the higher affinity and reactivity ferric complexes and their kinetic and theoretical studies are in progress.

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Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication CCDC 612365 for **1**. Copies of the data can be obtained *via* the Cambridge Crystallographic Data Centre (E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk/deposit).

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