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A Novel Cd(II) Complex with 1,3-bis(4-Pyridyl)propane: Synthesis, Crystal Structure, and Interaction with DNA[1]

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Abstract—The complex $[Cd(Bpp)_3Cl_2]_n \cdot 2H_2O$ (Bpp = 1,3-bis(4-pyridyl)propane) has been synthesized and characterized by elementary analysis, IR spectrum and singel-crystal X-ray diffraction. The crystal belongs to monoclinic system, space group $C2/c$ with the crystal cell parameters of a = 31.05(3), b = 17.556(13), c = 16.281(13) Å, β = 121.402(7)°, V = 7574(10) Å^3, and Z = 8. The compound has formed a 1D surface shape structure through these coordinate modes with the ligand. The 2D layers are further aggregated by hydrogen bonding with octameric subunits.

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INTRODUCTION

Synthetic coordination chemistry has underwent the rapid development during the past decades [1], Study in this field has provided numerous examples of rationally designed sundry coordination polymers possessing interesting structural motifs and significant properties in catalysis, gas adsorption, magnetism, DNA recognition, and so on [2–6]. In the crystal structure aspects, scientists not only pay attention to regular coordination bonds but also to weak interactions, such as hydrogen bonding, π–π–stacking, metal–metal and so on, because these weak interactions are important factors for diversity of supramolecular structure [7–10]. In bioactivity aspects, the interaction mechanism and antitumor activity between the complex and DNA molecule have been reported compre-hensively [11–14]. Flexible ligands may provide more possibilities for the construction of unique frameworks because of their freedom of conformation.

On the other hand, Cd(II)-containing coordination polymers have attracted considerable recent interest owing to the ambiability to form bounds with different dornors simulta-neously, the large radius, various coordination modes, and special physical properties of Cd^{2+} ion. To date, researchers have reported a number of 1D, 2D, or 3D Cd(II) coordination polymers. The flexible ligand 1,3-bis(4-pyridyl)propane (Bpp) has been, also, frequently used as a spacer for the construction of the polymeric compounds [15–18].

EXPERIMENTAL

Instruments and reagents. All the other chemicals and reagents were of reagent grade, which purchased from commercial sources and used without further purification except that the solvents used for physical measurements were purified by classical methods. The HeLa cells (human cervix epitheloid carcinoma) and KB cells (human oral epithelial carcinoma) applied here were obtained from the American Type Culture Collection and their DNA were extracted by ourselves. Elemental analyses (C, H, and N) were carried out on a model Finnigan EA1112 apparatus. IR spectra were recorded in KBr pellets on a Nicolet FT-IR 470 spectrometer. UV-Vis spectra was recorded on a Shimadzu UV-240 instrument, and fluorescence spectra were carried out on a Perkin Elmer LS55 fluorescence spectrometer.

Synthesis of complex $[Cd(Bpp)_3Cl_2]_n \cdot 2H_2O$ (I). $Cd(NO_3)_2$ (reagent grade) aqueous solution (10 mM, 10 mL), and (1,3-bis(4-pyridyl)propane) (10 mM, 10 mL) were mixed with stirring. Then a KOH solution (0.5 mM) was added to adjust pH until the turbid solution became clear at pH 7.63. The mixture was stirred for over 6 h and then the solution was left to evaporate at room temperature. After two weeks prim rose transparent crystals were obtained with the yield of 53.6%.

IR (ν, cm^{-1}): 3450 w, 2930 w, 2426 w, 1614 m,1560 w, 1486 w, 1429 m, 1384 s, 1297 s, 1227 s, 1069 w, 1021 w, 815 w, 617 w, 518 w.

For $C_{39}H_{46}N_6O_2Cl_2Cd$

anal. calcd., %:	C, 57.53;	H, 5.69;	N, 10.32.
Found, %:	C, 57.48;	H, 5.66;	N, 10.37.

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Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Formula weight	814.12
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	31.05(3)
b, Å	17.556(13)
c, Å	16.281(13)
β, deg	121.402(7)
V, Å$_3$	7574(10)
Z	8
ρ_{calcd}, g cm^{-3}	1.428
F(000)	3360
θ Range for data collection, deg	3.07–27.88
Limiting indices	$-40 \leq h \leq 40, -22 \leq k \leq 22, -21 \leq l \leq 21$
Reflections collected/unique	38527/8958 ($R_{int} = 0.1076$)
Completeness, %	98.8
Data/restraints/parameters	8958/6/463
Goodness-of-fit on F^2	1.101
Final R indices, $I > 2\sigma(I)$	$R_1 = 0.0759$, $wR_2 = 0.1981$
R indices, all data	$R_1 = 0.1015$, $wR_2 = 0.2237$
Δρ(max) and Δρ(min), e Å^{-3}	1.965 and −1.093

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I**

Bond	d, Å	Bond	d, Å
Cd(1)–N(1)	2.363(4)	Cd(1)–N(3)	2.371(4)
Cd(1)–N(5)	2.365(5)	Cd(1)–Cl(1)	2.581(2)
Cd(1)–N(4)	2.369(4)	Cd(1)–Cl(2)	2.585(2)
Angle	ω, deg	Angle	ω, deg
N(1)Cd(1)N(5)	90.37(15)	N(4)Cd(1)Cl(1)	90.59(12)
N(1)Cd(1)N(4)	176.66(15)	N(5)Cd(1)Cl(1)	88.94(12)
N(5)Cd(1)N(4)	88.73(15)	N(3)Cd(1)Cl(1)	87.93(12)
N(1)Cd(1)N(3)	88.85(15)	N(1)Cd(1)Cl(2)	89.26(13)
N(5)Cd(1)N(3)	176.73(15)	N(5)Cd(1)Cl(2)	92.90(12)
N(4)Cd(1)N(3)	92.22(15)	N(4)Cd(1)Cl(2)	87.58(13)
N(1)Cd(1)Cl(1)	92.61(13)	N(3)Cd(1)Cl(2)	90.27(12)
Cl(1)Cd(1)Cl(2)	177.37(5)		

X-ray structure determination. The crystal structure of complex **I** was determined by singel-crystal X-ray diffraction. A suitable single crystal was mounted in a glass fiber capillary. Data were collected on a Brucker Smart 1000 CCD X-ray singlecrystal diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 293(2) K with the ω scan technique. The structure was solved by direct methods and refined by the full matrix least squares procedures with SHELXTL-97 systems [19, 20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in ideal geometrical positions. A summary of the crystallographic data and structural parameters are listed in Table 1 and selected bond distances and angles are given in Table 2. Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 992422; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISSCUSSION

The crystal unit structure of complex $[Cd(Bpp)_3Cl_2]_n \cdot 2H_2O$ (**I**) was determined by X-ray crystallography as shown in Fig. 1. A single-crystal X-ray analysis revealed that complex **I** is self-assembled from 1D zigzag polymeric coordination chains. In the asymmetric unit of complex **I**, four nitrogen atoms from four Bpp ligands and two Cl molecules are coordinated to the Cd^{2+} ion. The coordination geometry of the Cd^{2+} ion closely resembles an octahedral environment with two oxygen atoms occupying mutually *trans* positions. The bipyridyl Bpp ligand was known to show four different conformations, and in this structure *trans-trans* for one Bpp ligand and *trans-gauche* for the other three Bpp ligands are present.

In compounds **I**, the Bpp ligands bridge Cd^{2+} ions to form one-dimensional chain compounds, and two halide ligands are also coordinated to Cd^{2+} ions (Fig. 2).

As is known to all that hydrogen bond is one of the key factors in the formation of coordination complex, thus supramolecular polymers was formed [21, 22]. Two adjacent 1D chains interact with each other through hydrogen bonds to form two-dimensional layered structure. There are two 'moderate' [23] hydrogen bonds, operating between O(1)–H(5B) 2.037 Å and O(3)–H(10) 2.439 Å, form a wide range of hydrogen bond network structure (Fig. 3).

The hydrolysis of complex **I** was studied by UV-visible absorption spectroscopy according to a literature method [24]; the spectra are illustrated in Fig. 4.

Electronic absorption spectroscopy is one of the most useful techniques for DNA-binding studies of metal complexes [25]. A complex binding to DNA through intercalation usually results in hypochromism and bathchromism, due to the intercalation mode involving a strong hydrogen bonds interaction between an aromatic chromophore and the base pairs of DNA.

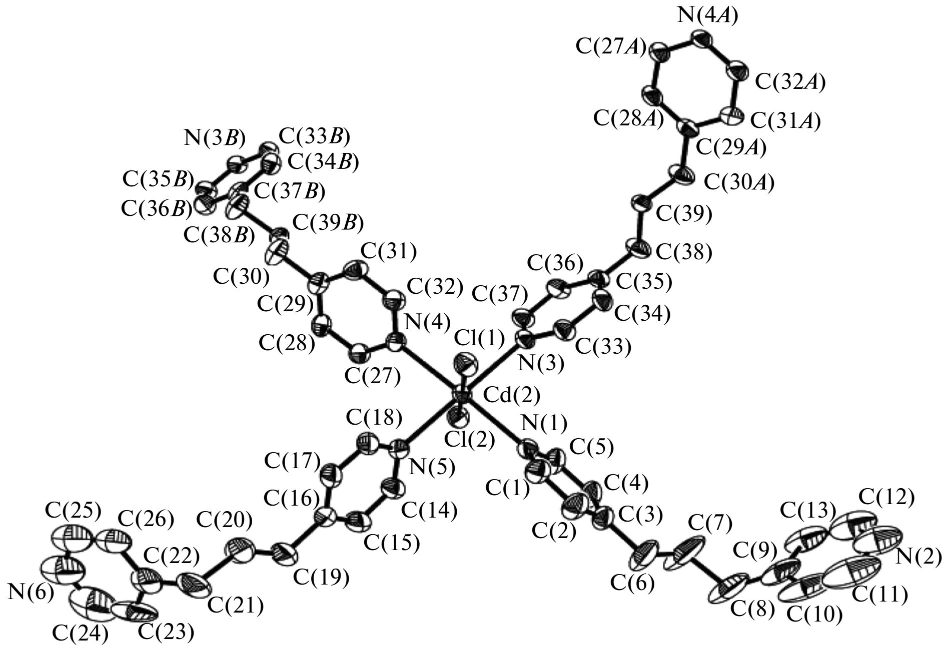

Fig. 1. Perspective view of the coordination environment of the cadmium atom in complex **I** (all hydrogen atoms of crystaline water were omitted for clarity).

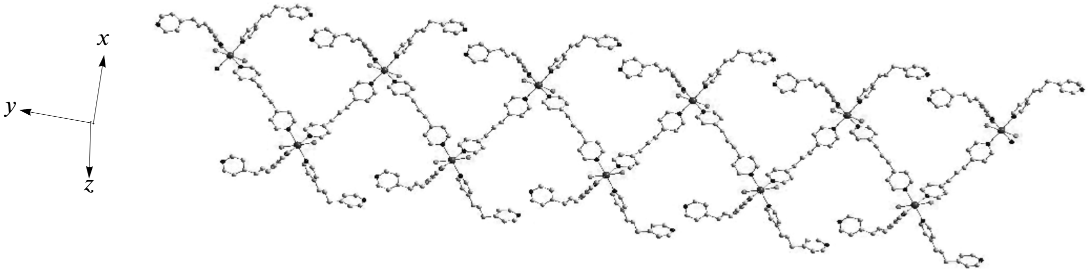

Fig. 2. 1D cadmium polymeric chain.

It seems to be generally accepted that the extent of the hypochromism in the UV band is consistent with the strength of intercalative interaction [26–29].

The absorption spectra of Cd(II) and Bpp complexes in the absence and presence of FS–DNA ([complex] = 20.0 μM, $[\mathrm{DNA}]_{1/4}$ 0–48.0 μM) are given in Fig. 4. The intense absorption bands around 200 and 350 nm reveal the intraligand hydrogen bonds of Bpp. Addition of increasing amounts of FS–DNA resulted in a reduction in absorbency and slight red shift in the UV spectra of the complexes. This phenomena is attributed to the strong stacking interaction between aromatic group and the base pairs of FS–DNA when the complexes intercalate to the FS–DNA. In order to show the intensity between the complexes and FS–DNA, the intrinsic binding constant K of the complexes with FS–DNA are determined according to the following equation [30].

Ethidium bromide (EtBr) is a planular molecule and it was shown to emit intense fluorescence light in the present of DNA, due to its strong intercalation between the adjacent DNA base pairs and EtBr. In a previous study, the fluorescent light could be quenched by the addition of the complex which can compete with EtBr to bind with DNA. This is a proof that the complexes intercalate to base pairs of DNA [31–33]. The quenching extent of fluorescence of EtBr–DNA is used to determine the extent of binding between the complex and DNA.

The emission spectrum of EtBr bind to DNA in absence and in the presence of the title complex is given in Fig. 5. From Fig. 5, we know that the addition of the title complex to DNA pretreated with EtBr causes appreciable reduction in the emission intensity, indicating that replacement of the EtBr by the title complex [34, 35]. The finding is consistent with electronic absorption titration results, both indicated that the title complex bind to DNA in an intercalative

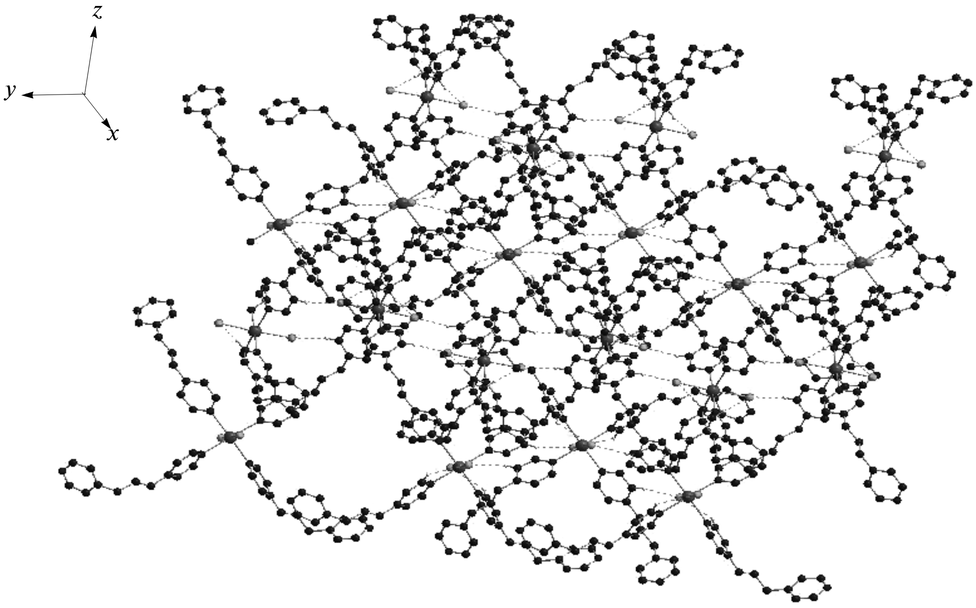

Fig. 3. 2D structure of complex **I** formed through hydrogen bonds.

mode, this is quite different from the binding of Cd(II) complexes with DNA, which is linked by N(7) atoms of adjacent purine bases of DNA and form intrastrand cross-links [36, 37].

Efficiencies of the complexes binding to DNA are compared quantitatively, according to the classical Stern–Volmer equation: $I_0/I = 1 + K_{sq}r$, where I_0 and I represent the fuorescence intensity in the absence and presence of the complex, respectively, and r is the concentration ratio of the complex to DNA. K_{sq} is a linear Stern–Volmer quenching constant dependent on the ratio of the bound concentration of EtBr to the concentration of DNA [38]. The K_{sq} value is obtained as the slope of I_0/I versus linear plot. The fuorescence-quenching curves of DNA-bound EtBr in the absence and presence of the two complexes are given in Fig. 6.

Thus, a new Cd(II) complex $[Cd(Bpp)_3Cl_2]_n \cdot 2H_2O$ has been synthesized and characterized. The crystal structure of the complex was determined by single crystal X-ray diffraction. The DNA-binding properties of the complex were examined by absorption and fluorescence spectra. This study on the synthesis and crystal structure of complex **I** provides important information which could help to understand the mechanism of activity of the cadmium complexes interacting with DNA. Thus the newly synthe-

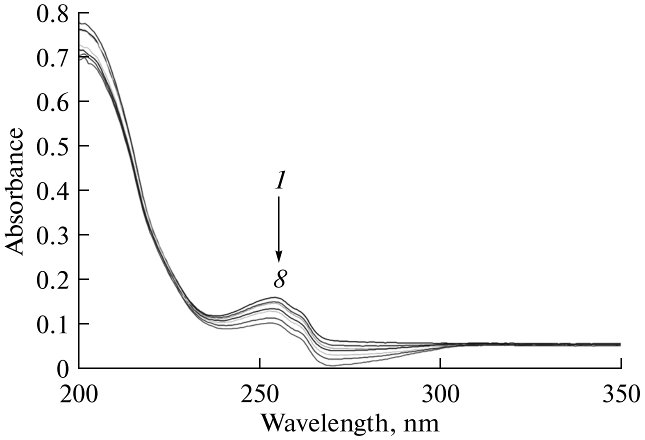

Fig. 4. The hydrolyzation reaction UV spectrum for complex **I**.

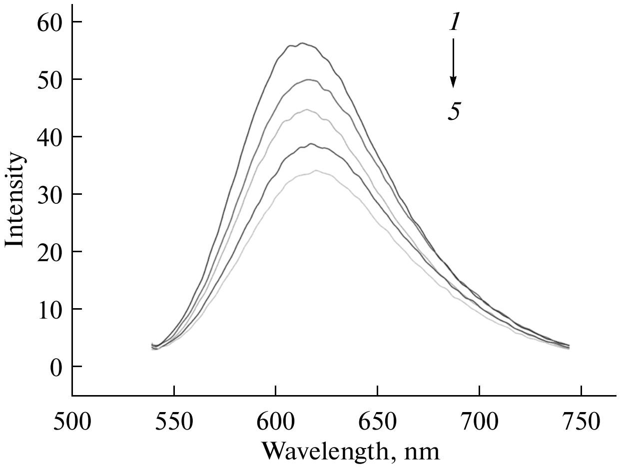

Fig. 5. Emission spectrum of EtBr bound to DNA in the presence of four complexes. The arrow shows the intensity changes on increasing thecomplexes concentration.

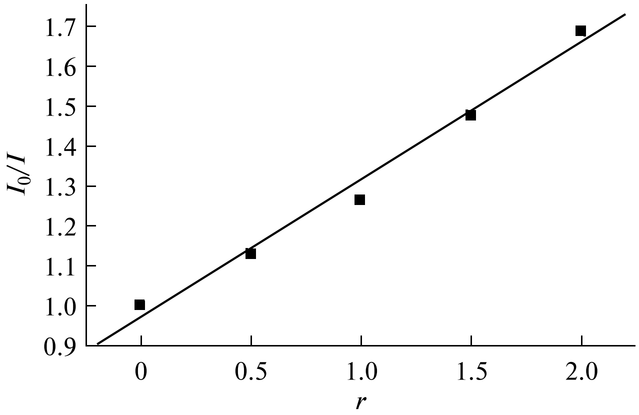

Fig. 6. Stern–Volmer quenching plots of complex **I** with the value of slope being 0.3438.

sized Cd(II) complex may be potential antitumor agent due to its unique interaction mode with DNA.

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