

Research Article

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Synthesis, structure, DNA binding and anticancer activity of a new tetranuclear Pb(II) complex constructed by 8-hydroxyquinolate and 4-nitrobenzoate ligands

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Abstract: A new Pb(II) complex, [Pb(8-OQ)(4-NB)], where 8-OQ = 8-hydroxyquinolate, 4-NB = 4-nitrobenzoate, has been synthesized and characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. The single crystal X-ray analysis reveals that the complex possesses a tetranuclear Pb_4O_4 cubane structure. The Pb(II) atom is coordinated by three triply bridging phenolic hydroxyl O atoms of 8-OQ ligands, then the tetranuclear Pb system is formed resulting in a tetrahedral cage. The interaction of complex with HS-DNA in Tris buffer was studied by UV–vis absorption spectrum and fluorescence ethidium bromide displacement experiment with an intrinsic binding constant of $1.52 \times 10^4 \text{ M}^{-1}$ and a linear Stern–Volmer quenching constant of $6.77 \times 10^3 \text{ M}^{-1}$. Anticancer activity against MCF-7, HepG-2 and A549 cell lines of complex was also determined by the MTT-based assay. The results showed the complex can inhibit proliferation of these three kinds of tumor cells and is less cytotoxic than cisplatin.

Keywords: Pb(II); 8-hydroxyquinolate; 4-nitrobenzoate; crystal structure; DNA-binding; anticancer activity

1 Introduction

Polynuclear coordination compounds have attracted more and more attention in the past thirty years due to their beautiful, highly-symmetrical structures coupled with their potential applications in catalysis, magnetism, luminescence, photoactivity, and bioactivity (Armaroli, 2001; Lin et al., 2009; Nesterov et al., 2018; Thompson, 2002; Yam and Lo, 1999; Yilmaz et al., 2014). Among the polynuclear coordination compounds, some complexes have cage structure with tetrahedra, cubes, truncated tetrahedra and tetra-capped truncated tetrahedra configurations (Henkel et al., 1987; Ward, 2009). 8-Hydroxyquinoline and 8-hydroxyquinoline derivatives, as excellent ligands with O- and N- donor, especially, the O- donor can display the mono-, bi- and tri-dentate coordinate modes; take an important role in constructing the polynuclear complexes and polynuclear coordination cages (Aromí, et al., 2003; Cheng et al., 2010; Yuan et al., 2013; Zhang et al., 2014). Pb(II) ion, having a large metal centre, can adopt many different ligands and form compounds with flexible coordination numbers as well as novel structures (Cheng et al., 2014a; Cheng et al., 2014b; Cockrell et al., 2008; Fan and Zhu, 2007; Farina et al., 2013; Mah and Jalilvand, 2012; Zhang and Zhu, 2008). Several polynuclear Pb(II) 8-hydroxyquinoline complexes have been reported previously (Aslani and Morsali, 2008; Fard and Naraghi, 2013; Ghaemi et al., 2012; Jennifer and Muthiah, 2014). Herein we report a new tetranuclear Pb(II) coordination cage synthesized with the 4-nitrobenzoic acid introduced into the system of Pb^{II} /8-hydroxyquinoline. In recent years, a few Pb(II) complexes have been reported concerning their biological activities, such as DNA binding property (Gao et al., 2017; Li et al., 2008; Shen et al., 2016; Zhang et al., 2015), anticancer (Abd-Elzaher et al., 2012; Ghosh et al., 2017) and antimicrobial (El-Megharbel et al., 2014; Kurtaran et al., 2005; Pallikkavil et al., 2013;

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Ravichandran et al., 2014; Singh et al., 2010) activity. In this paper, in addition to the complex was characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction, as an attempt, the interaction between the complex, [Pb(8-OQ)(4-NB)], and DNA was investigated by UV absorption and fluorescence spectra, anticancer activity against MCF-7, HepG-2 and A549 cell lines of the complex was also tested by the MTT-based assay.

2 Result and discussion

2.1 Structure analysis

The structure of the complex was determined by single crystal X-ray diffraction. As shown in Figure 1, the complex crystallizes in the tetragonal system with I41/a space group, exhibiting monomeric species with one lead atom, one 8-hydroxyquinolinate anion, and one 4-nitrobenzoate anion in an asymmetric unit. Each Pb1 is six-coordinated by three triply bridging phenolic hydroxyl O atoms of 8-OQ and each phenolic hydroxyl O atom bridges to three Pb^{II} cations; thus, it forms a distorted tetranuclear cuboidal Pb₄O₄ core which has S₄ site symmetry with each Pb^{II} ion occupying the alternating corner. Every two adjacent Pb atoms in the Pb₄O₄ core are linked by dashed line (Figure 2), resulting in a tetrahedral cage with C₃ symmetry. In the Pb₄O₄ unit, four carboxylate groups from 4-NB ligands chelate to the four Pb^{II} ions and expand to four different orientations; at the same time, another four N atoms of 8-OQ are monodentate to the four Pb^{II} ions. The Pb-O and Pb-N bond lengths and selected angles are listed in Table 1. Within the Pb₄O₄ unit, the Pb...Pb distance is 4.0553(1) Å, the O-Pb-O angles are 71.83(16) and 70.32(15)°, and the Pb-O-Pb angles vary from 103.39(17) to 109.37(17)°. Moreover, there is a clearly significant gap surrounding the lead atom, suggesting that the 6s² lone pair electrons of Pb^{II} are stereochemically active (Janiak et al., 2000; Shimoni-Livny et al., 1998) (Figure 1).

2.2 DNA binding studies

The UV-Vis spectroscopy is an effective method to determine the binding strength and the mode of DNA binding with the metal complex. The UV-vis absorption spectra of the complex are carried out to test the bonding ability with HS-DNA and shown in Figure 3. The peaks at 240 nm and 257 nm of the complex exhibit hypochromism of about 8.03% and 7.18% respectively, without red shift

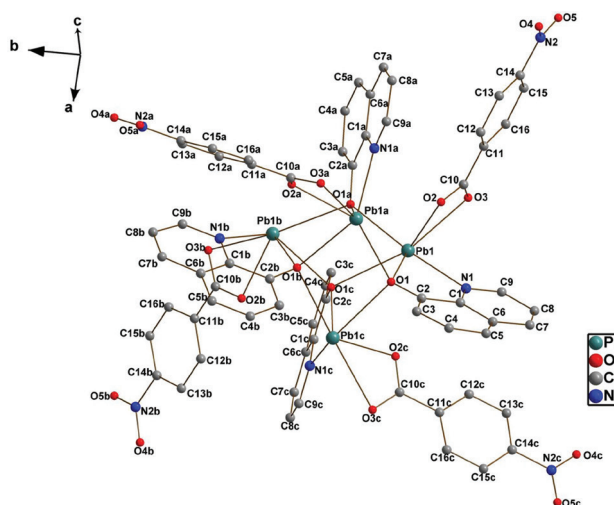


Figure 1: A view of the molecular structure of complex. Hydrogen atoms are omitted for clarity.

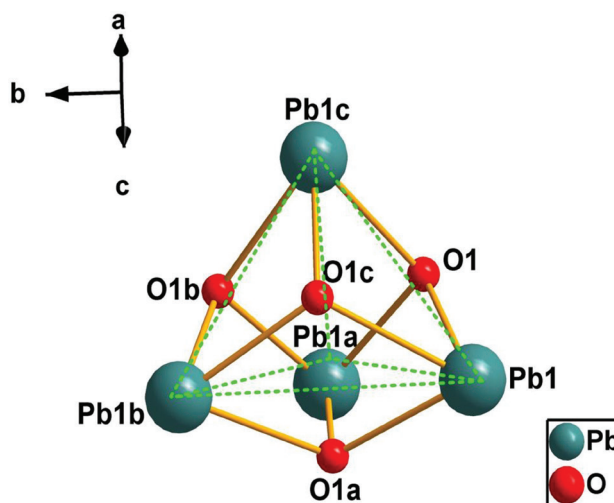


Figure 2: A view of Pb₄O₄ core (adjacent Pb atoms linked by green dashed line).

in the band position, which indicates that the complex binds to DNA through the groove binding mode over intercalative binding mode (Loganathan et al., 2015). To quantitatively evaluate the binding magnitude between the complex and HS-DNA, the intrinsic binding constant K_b was determined by the following equation (Pyle et al., 1989):

$$\frac{[DNA]}{\varepsilon_a - \varepsilon_f} = \frac{[DNA]}{\varepsilon_b - \varepsilon_f} + \frac{1}{K_b(\varepsilon_b - \varepsilon_f)} \quad (1)$$

The binding constant (K_b) was obtained to be $1.52 \times 10^4 \text{ M}^{-1}$.

In order to further clarify the interaction between complex and HS-DNA, the ethidium bromide (EB) fluorescence displacement experiment has been performed. In presence of DNA, the fluorescence intensity of EB will be enhanced due to its intercalative binding to

Table 1: Selected bond lengths (Å) and angles (deg) for the compound.

Pb1-O1	2.320(5)
Pb1-O2	2.425(5)
Pb1-O3	2.717(6)
Pb1-N1	2.444(7)
Pb1-O1 ⁱ	2.752(5)
Pb1-O2 ⁱⁱ	2.832(5)
O1-Pb1-O2	83.75(17)
O1-Pb1-O3	130.33(16)
O1-Pb1-N1	70.3(2)
O1-Pb1-O1 ⁱ	71.83(16)
O1-Pb1-O1 ⁱⁱ	70.32(15)
O2-Pb1-O3	50.76(15)
O2-Pb1-N1	77.3(2)
O2-Pb1-O1 ⁱ	70.81(16)
O2-Pb1-O1 ⁱⁱ	137.76 (16)
O3-Pb1-N1	79.9(2)
O3-Pb1-O1 ⁱ	104.42(16)
O3-Pb1-O1 ⁱⁱ	156.95(14)
N1-Pb1-O1 ⁱ	132.36(19)
N1-Pb1-O1 ⁱⁱ	121.02(19)
O1 ⁱ -Pb1-O1 ⁱⁱ	69.69(15)
Pb1-O1-Pb1 ⁱ	103.39(17)
Pb1-O1-Pb1 ⁱⁱ	105.84(18)
Pb1 ⁱ -O1-Pb1 ⁱⁱ	109.37(17)

Symmetry code: (i) 3/4-x, -3/4+y, 3/4-z; (ii) 3/4+x, 3/4-y, 3/4-z.

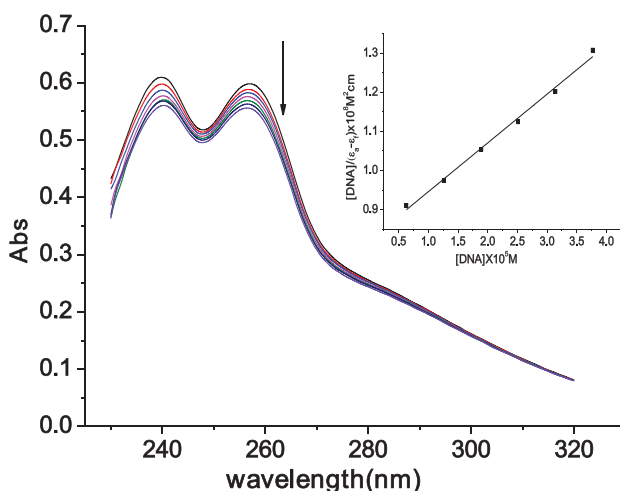


Figure 3: Electronic absorption spectra of the complex upon the titration of HS-DNA. Arrow indicates the change upon increasing the DNA concentrations. Inset: $[DNA]/(\epsilon_a - \epsilon_f)$ vs. $[DNA]$.

DNA. The fluorescence intensity of EB can be quenched by the addition of complex due to the displacement of EB from DNA. As shown in Figure 4 the fluorescence intensity decrease gradually on progressive addition of the complex, suggesting that it was competing effectively with the intercalated EB molecule for occupied binding sites on DNA by replacing EB. The Sterne-Volmer quenching constant K_{sv} was calculated using Sterne-Volmer equation (Lakowicz and Weber, 1973):

$$\frac{I_0}{I} = 1 + K_{sv} [Q] \quad (2)$$

I_0 and I are the emission intensities in the absence and presence of the complex (as a quencher), respectively, K_{sv} is the Stern–Volmer quenching constant, $[Q]$ is the quencher concentration. From fFigure 4, with the quenching plot of I_0/I versus $[complex]$, K_{sv} is given by the ratio of the slope to intercept and then K_{sv} value for the complex is $6.77 \times 10^3 \text{ M}^{-1}$.

2.3 Anticancer activity

To investigate the anti-cancer effects of complex in vitro, we examined the effect of the complex on the proliferation of HepG-2, MCF-7 and A549 cell lines using the MTT assay. The three tumor cells were treated with the tested complex and incubated for 48 h at increasing concentration. The IC₅₀ values for HepG-2, MCF-7 and A549 cell lines were 113 ± 9 , 140 ± 11 and $96 \pm 7 \mu\text{M}$, respectively. It is clear that compound showed better activity against A549 cell line than the other two cancer cells, but displayed lower inhibitory action to the three cell lines than the clinically

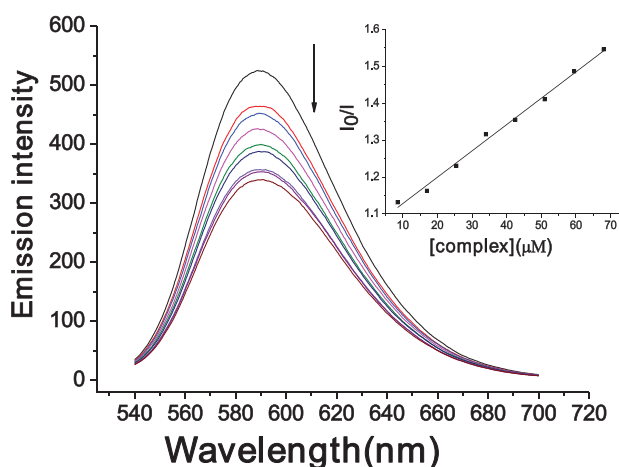


Figure 4: Emission spectra of the HS-DNA-EB system upon titration of the complex. Arrow shows the change upon increasing complex concentration. Inset: I_0/I vs. $[complex]$.

practiced antitumor drug cis-platin, the IC₅₀ values of cis-platin (Zhao et al., 2013) are 0.6 ± 0.02 , 3.6 ± 0.2 and 4.3 ± 0.2 μM to HepG-2, MCF-7 and A549 cell lines.

3 Conclusion

In summary, one new Pb(II) complex based on mixed ligands of 8-Hydroxyquinoline and 4-nitrobenzoic acid, has been synthesized and structurally characterized. The structure of the complex has been determined by X-ray crystal analysis. The tetranuclear Pb structure and a tetrahedral cage are achieved by the three triply bridging phenolic hydroxyl O atoms of 8-hydroxyquinolate anions. The DNA binding properties of the complex were examined by UV-vis absorption spectrum and fluorescence ethidium bromide displacement experiment. The intrinsic binding constant is calculated as $1.52 \times 10^4 \text{ M}^{-1}$ and the linear Stern-Volmer quenching constant of EB bound to DNA by the complex is $6.77 \times 10^3 \text{ M}^{-1}$. Anticancer activity against MCF-7, HepG-2 and A549 cell lines of complex was also tested. The results showed the complex can inhibit proliferation of these three tumor cells, but less cytotoxic than cisplatin.

Experimental

General

All reagents were purchased commercially and used without further purification. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with a Perkin-Elmer 2400II element analyzer (PerkinElmer, Waltham, MA, USA). Fourier transform IR (FTIR) spectra were recorded on a Nicolet-iS10 spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) (range, 400-4000 cm^{-1}) as KBr pellets. Crystal structure was determined on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector (Agilent Technologies Inc, Santa Clara, CA, USA).

Preparation of [Pb(8-OQ)(4-NB)]

A mixture of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (0.191 g, 0.50 mmol), 8-hydroxyquinoline (0.0363 g, 0.25 mmol) and 4-nitrobenzoic acid (0.1671 g, 1.0 mmol) in a DMF/ H_2O (2:1) solution (30 mL) was refluxed for 4 h and filtered. Yellow

block crystals were obtained after 21 days. Yield: 32.81% based on 8-hydroxyquinoline. Elemental analysis calcd. (%) for $\text{C}_{64}\text{H}_{40}\text{N}_8\text{O}_{20}\text{Pb}_4$: C, 37.11; H, 1.95; N, 5.42. Found: C, 37.17; H, 1.90; N, 5.45. IR (KBr, cm^{-1}): 3054w, 1548s, 1496s, 1459s, 1388s, 1343s, 1315s, 1269m, 1238w, 1135w, 1102s, 1011w, 877w, 832s, 787m, 755m, 725s, 644w, 604w, 519m, 498m.

X-ray crystallography

Single-crystal X-ray diffraction data was obtained using Agilent SuperNova diffractometer equipped with an Atlas CCD detector at 144.41(16) K with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$). The structure was solved by direct methods using SHELXT-2014 (Sheldrick, 2015a) and refined by full matrix least squares with SHELXL-2014 (Sheldrick, 2015b), refining on F^2 . Selected bonds and angles are given in Table 1. Detailed crystal data and structure refinement are listed in Table 2. Crystallographic data has been deposited with the Cambridge Crystallographic Centre as supplementary publication number CCDC-1858154.

DNA-binding experiments

The stock solution of HS-DNA was performed in a buffer solution (containing 5 mM Tris/50 mM NaCl at pH 7.2) followed by stirring for 1 h. The stock solution of HS-DNA was stored at 4°C and used in not more than one week. The buffer solution of HS-DNA gave a ratio of UV absorbance at 260 and 280 nm (A_{260}/A_{280}) of 1.82, indicating that the DNA was free from protein (Marmur, 1961) HS-DNA concentration was determined by the absorption spectroscopy using $\epsilon_{260} = 6600 \text{ M}^{-1}\text{cm}^{-1}$ (Reichmann et al., 1954). The complex was prepared by dissolving the complex in DMSO and diluted suitably with Tris-HCl buffer to required concentrations for all the experiments.

In the measurement of UV spectra, the concentration of the complex was constant while varying HS-DNA concentration. UV spectra were recorded in the range of 200-400 nm about 5 min after each addition of DNA solution. The intrinsic binding constant, K_b , for the interaction of compound with DNA has been determined using the UV spectra of the complex.

In the EB fluorescent displacement assay, 5 μL of the EB Tris-HCl solution ($1.0 \text{ mmol}\cdot\text{L}^{-1}$) was added to 1 mL of DNA solution in Tris-HCl/NaCl buffer solution at pH 7.5. The competitive EB binding studies of the complex

Table 2: Crystal data and Refinement Parameters.

Empirical formula	C ₁₆ H ₁₀ N ₂ O ₅ Pb
Formula weight	517.45
Crystal dimensions(mm)	0.20×0.22×0.25
Crystal system	Tetragonal
Space group	I41/a
a(Å)	17.0086(7)
b(Å)	17.0086(7)
c(Å)	22.0999(12)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å ³)	6393.6(6)
Z	16
Dc(g·cm ⁻³)	2.150
μ(mm ⁻¹)	10.584
F(000)	3872
T(K)	144.41(16)
λ(Å)	MoKα(0.71073)
θ Range(°)	3.7–25.00
Absorption correction	multi-scan
T _{max} and T _{min}	1.00000 and 0.11253
Measured reflections	7808
Unique reflections	2817
Observed reflections	2292
No. of parameters refined	217
R1,WR2[>2σ(I)]	0.0411,0.0931
R1,WR2[all data]	0.0561,0.1018
GOOF	1.02
Largest peak and hole(e·Å ⁻³)	2.66, -3.31

was investigated in the range of 540–700 nm (510 nm excitation) with gradual addition of complex solution into the solution of the DNA–EB system.

MTT-based anticancer activity test

Standard MTT assay procedures were performed for testifying anticancer activity. Cancer cells MCF-7, HepG-2 and A549 were seeded in 100 ml complete medium in each well of 96-well culture plates (1×10^4 cells per well) for overnight at 37°C and 5% CO₂. The tested complex was dissolved in DMSO, and diluted to obtain desired concentrations in culture medium before use. This solution was added to cells of tested well in triplicate and incubated

as per experimental design. Upon completion of the incubation, the prepared MTT solution (100 μL, 0.5 mg/ml of media without phenol red and serum) was added to each well. The plates were incubated for a further 4 h at 37°C, then the culture medium was discarded from each well and 200 μL DMSO was added to dissolve the MTT for 10 min at 37°C. The absorbance was recorded on a microplate reader at a wavelength of 490 nm. the values of IC₅₀ for these cell lines were measured by plotting the percentage cytotoxicity versus concentration on a logarithmic graph.

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