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Structure and antibacterial property of coordination polymer $[Ni_2(en)_4Cl_2]Cl_2$

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Complex $[Ni_2(en)_4Cl_2]ClV2$ (1) was synthesized for the first time through solvothermal synthesis by ethylenediamine (*en*) and Ni(II) ion. Complex 1 exhibits a zero-dimensional (0D) structure, which is linked into a three-dimensional (3D) supramolecular network through hydrogen bonds N–H·Cl. Moreover, the antibacterial property of complex 1 was tested. The antibacterial properties against Gram-negative bacteria are slightly better than against Gram-positive bacteria in complex 1.

Keywords: hydrogen bond; supramolecular structure; antibacterial property.

Структура та антибактеріальні властивості координаційного полімеру $[Ni_2(en)_4Cl_2]ClV2$]. *Yanan Luo, Miao Kong, Pengfei Wang, Kangming Liu, Zhengyu Yang, Yutong Wang*

Комплекс $[Ni_2(en)_4Cl_2]ClV2$ (1) вперше синтезовано методом сольвотермічного синтезу під дією етилендіаміну (*en*) та іона Ni(II). Комплекс 1 демонструє нуль-розмірну (0D) структуру, яка пов'язана у тривимірну (3D) супрамолекулярну мережу за допомогою водневих зв'язків N–H·Cl. Визначено антибактеріальні властивості комплексу 1. Антибактеріальні властивості до грамнегативних бактерій трохи краще, ніж до грампозитивних бактерій у комплексі 1.

Комплекс $[Ni_2(en)_4Cl_2]ClV2]$ (1) впервые синтезирован методом сольвотермического синтеза под действием этилендиамина (*en*) и иона Ni(II). Комплекс 1 демонстрирует нульмерную (0D) структуру, которая связана в трехмерную (3D) супрамолекулярную сеть посредством водородных связей N–H·Cl. Определены антибактериальные свойства комплекса 1. Антибактериальные свойства по отношению к грамотрицательным бактериям немного лучше, чем к грамположительным бактериям в комплексе 1.

1. Introduction

Metal-organic coordination polymers, as multifunctional materials, are a new type of crystalline materials which are obtained through a combination of inorganic material chemistry and coordination chemistry. These crystalline materials have attracted attention for their novel structure and potential applications in the fields of fluorescence, gas adsorption, catalysis, molecular recognition and as antimicrobial agents [1–4]. The central metal ion and organic ligand are the two crucial basic units in the metal-organic coordination polymers. Therefore, the choice of the two crucial basic units is important for the construction of a unique complex. In recent years, the researchs on organic ligands has gradually increased, and many kinds of organic ligands (such as or-

ganic ligands containing N and O atoms) have been widely used in the construction of metal-organic coordination polymers [5, 6]. Ethylenediamine *(en)* is a typical nitrogen-containing organic ligand, which has attracted the interest of many researchers because of its flexible skeleton structure and strong coordination ability. Long-term research has shown that the complexes formed by *en* are not only stable in structure, but also usually contain many hydrogen bonds, which can bind the complexes to form supramolecular complexes with high-dimensional spatial configuration [7–9]. Therefore, *en* has been widely used in the construction of metal-organic coordination polymers [10, 11]. In addition, transition metal ions, especially Ag^{+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}, have their own unique properties. When they are the central ions of the complexes, the complexes have antibacterial properties [12]. It is worth noting that the metal complexes have been shown to have the properties of slowly releasing metal ions and the function of providing specific sites, which can be used as antimicrobial agents in the field of medicine [13]. The complexes formed by transition metal ions and *en* ligand not only form rich structures, but also make it possible to widely use them in various fields [14].

In this paper, we have solvothermally synthesized a new supramolecular complex, $[Ni_2(en)_4Cl_2]ClV2$ (1), the crystal structure of which has not been reported. The crystal structure of complex 1 was determined by single crystal X-ray diffraction. Then, complex 1 was characterized by elemental analysis, thermogravimetric analysis and powder X-ray diffraction. Finally, the antibacterial properties of complex 1 solution were successfully tested using the bacteriostatic circle method and the growth curve method.

2. Experimental

Synthesis of $[Ni_2(en)_4Cl_2]ClV2$ (1). A mixture of $F2[Ni_2(en)_4Cl_2]ClV2$ (60 mg, 0.463 mmol), en (0.05 mL), ethanol (2 mL) and DMF (15 mL) was dissolved in 50 mL beaker for 60 min at room temperature. The suspension was put into a Teflon-lined autoclave and kept under autogenous pressure at 100°C for 3 days. After slow cooling to room temperature, red acicular crystals were filtered and washed with DMF and dried in air with a yield of about 39 % (based on Ni). Analogously calculated for $C_8H_{32}Ni_2N_8Cl_4$ (499.64 g/mol): C 19.28; H 6.47; N 22.41 %; found: C 19.23; H 6.47; N 22.43 %.

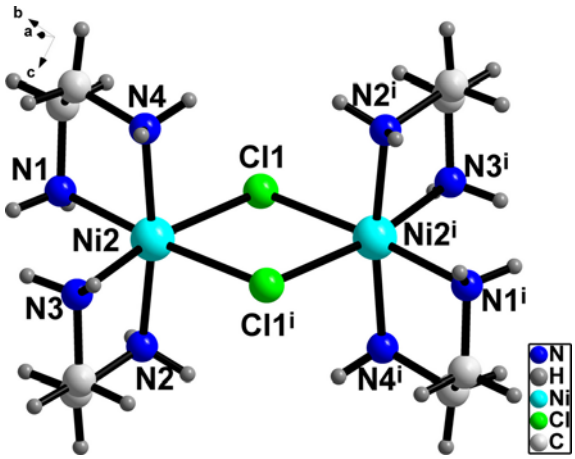

Fig. 1. The asymmetric structural unit of complex 1 (symmetry code: i, $-x$, $-y$, $-z$).

Structure determination. Complex 1 was stable under ambient conditions and single crystals were glued on thin glass fibers. Diffraction intensities were recorded on a Bruker Apex II CCD area-detector diffractometer (Mo Kα, 0.071073 nm). An empirical absorption correction was applied to the date using the SADABS program. The structure was determined by the direct method (SHELXS-97) and refined by full matrix least squares [15]. All non-hydrogen atoms were located anisotropically. All hydrogen atoms were located geometrically accoring the program OLEX-2 [16]. The final formula was derived from crystallographic data combined with elemental and thermogravimetric analyses data. CCDC-2073398 contains the supplementary crystallographic data for this paper.

Antibacterial tests. For antibacterial circle experiment, the following solution was used. The organic ligand *(en)* solution with the concentration of 2.5 mg/mL was prepared by ultrasonic stirring of 50 mg organic ligand in 10 mL distilled water. About 50 mg of the synthesized complex 1 was stirred in 5 mL of distilled water by ultrasonic agitation to prepare a complex 1 solution with a concentration of 10 mg/mL (Solution 1). 2.5 mL of solution 1 was taken into 2.5 mL of distilled water and ultrasonically stirred into a complex solution of 5 mg/mL (solution 2). Then 1.5 mL of solution 2 was taken into 1.5 mL distilled water and ultrasonically stirred into a complex solution of 2.5 mg/mL (solution 3).

The treatment of filter paper: Filter papers with a diameter of about 6 mm were placed into sterile distilled water, organic

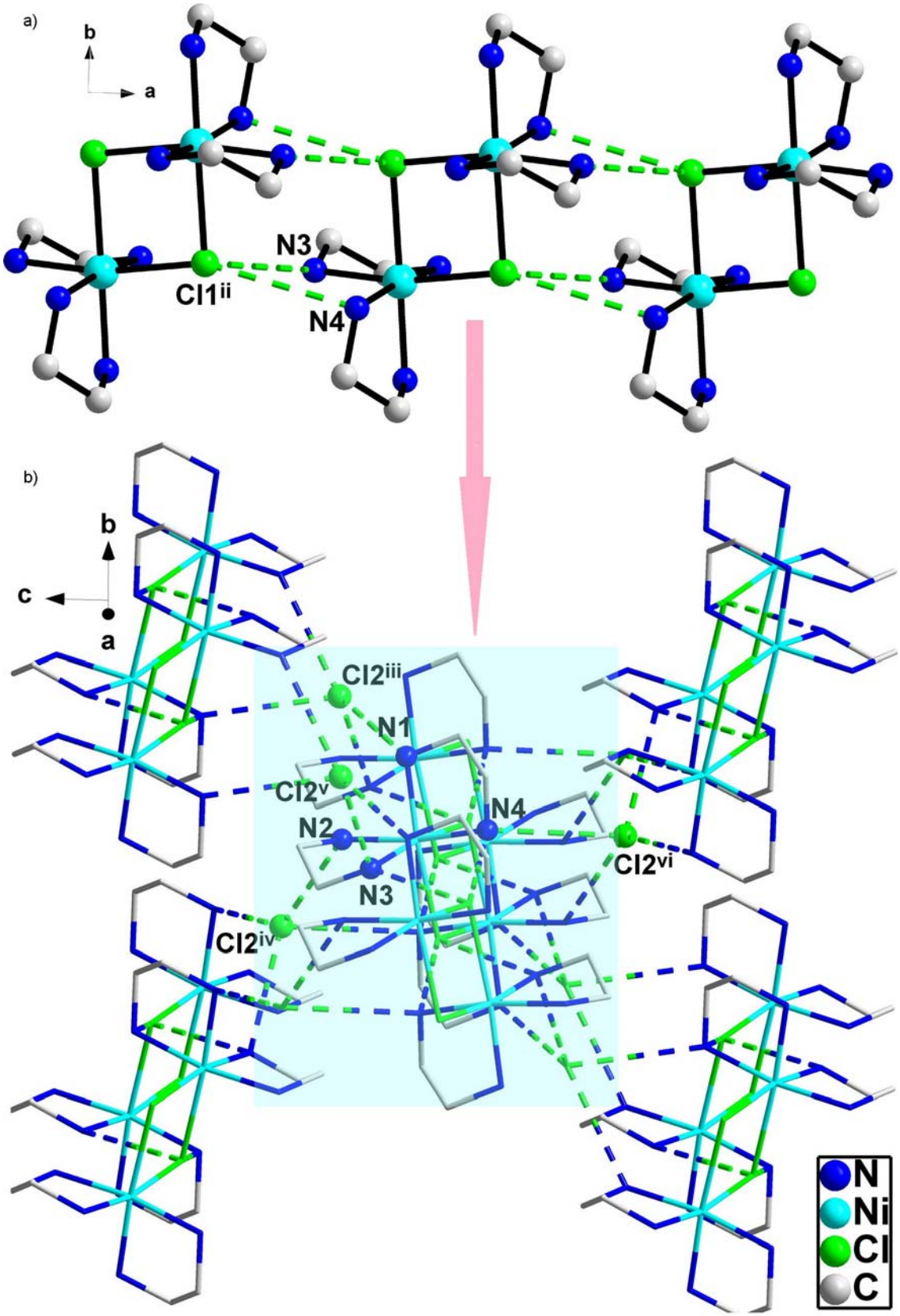

Fig. 2. (a) 1D structure of complex 1 via hydrogen bond interactions; (b) 3D supramolecular structure via hydrogen bond interactions (symmetry codes: ii, 1 + x, y, z; iii, −0.5 + x, 0.5−y, −0.5 + z; iv, −x, −y, 1−z; v, 0.5 + x, 0.5−y, −0.5 + z; vi, x, y, −1 + z. All hydrogen atoms are omitted for clarity)

Table 1. Complex 1 of crystal data collections and structure refinements

Complex 1			
Formula	$C_8H_{32}Ni_2N_8Cl_4$	Fw	499.64
Crystal system	Monoclinic	V/nm^3	1.0038(11)
Temperature,,K	296(2)	Space group	$P21/n$
α, °	90.00	ρ_{calc}, Mg·m^{-3}	1.653
β, °	94.18	μ, mm^{-1}	2.415
γ, °	90.00	Reflections collected	5150
a, nm	0.6333(4)	Z	2
b, nm	1.1304(7)	F(000)	520
c, nm	1.4059(9)	θ range, °	2.31–25.50
Final $R^{a,b}$ indices	R_1 = 0.0212	R indices (all data)	R_1 = 0.0222
[$I > 2\sigma(I)$]	wR_2 = 0.0542		wR_2 = 0.0551
Independent reflections (R_{int})	1872 (0.0175)	GOF	1.054

solvent solutions (*en*), solution 1, solution 2 and solution 3 respectively for ultrasound treatment. After soaking for 1 h, they were taken out and placed in a clean petri dish. Then they were placed on the aseptic operating table and irradiated by an ultraviolet lamp for sterilization. The disc diffusion method was used to determine the inhibition zones in the growth of bacterial species. Escherichia coli (ATCC25922) and Staphylococcus aureus (ATCC6538) were selected and inoculated into sterile nutrient agar. After the nutrient agar medium was cooled and shaped, filter paper of the treated blank water sample, ligand (*en*), solution 1, solution 2 and solution 3 were placed in a fixed position. The cultivation was carried out in an incubator at a constant of 37°C for 2–3 days and observed every 6 h.

Gram-growth curve experiment: Complex 1 of different weights was dissolved in the sterilized liquid medium, sealed and stirred by ultrasound. Medium solutions containing complex 1 at concentrations of 0, 25, 50, 100, 200, 400 and 800 μg/mL were placed in a sterile platform for UV irradiation for sterilization. A certain amount of Escherichia coli culture was inoculated into the liquid medium with the same volume and different concentrations (0, 25, 50, 100, 200, 400 and 800μg/mL) of complex 1, and placed in an incubator of 37°C for shock culture. At 0, 3, 6, 9, 12, 16, 18, 21 and 24 h, the absorbance of the above solution (including the same volume of Escherichia coli and different concentrations of complex 1) at fixed wavelength of 600 nm (according to the literature) was measured by an UV-Vis spectrophotometer [17].

3. Results and discussion

Single-crystal X-ray diffraction analysis reveals that complex 1 crystallizes in a monoclinic system, space group $P21/n$, which exhibits a zero-dimensional (0D) structures (Table 1). In addition, an asymmetric structural unit of complex 1 contains a Ni(II) ion, an *en* ligand molecule, a coordinated chlorine anion, and a free chlorine anion (Fig. 1).

The Ni(II) ion is coordinated by six atoms: four nitrogen atoms and two chloride anions. Here, Ni2 is coordinated by N1, N2, N3 and N4 from two different *en* molecules respectively, and Cl1 and Cl1^{i}, forming a slightly twisted octahedral structure. In complex 1, the *en*-ligand was in the chelation coordination mode. The two coordination Cl anions have a bridging coordination mode, and two Ni2 ions were linked to form a four-membered ring structure of Ni_2Cl_2 clusters (Fig. 1). In addition, the bond angle range of Ni2 is [82.37(6)–175.36(4)°]. The distances range of Ni2–Cl and Ni2–N is [0.2083(2)–0.2554(4) nm] (Table 2).

In complex 1, the 0D structure is connected into a three-dimensional supramolecular network structure through hydrogen bonds. Among them, N3 and N4 atoms in *en*-molecule are connected with adjacent Cl1^{ii} anion, forming a one-dimensional (1D) chain structure (Fig 2(a)). In addition, free chloride ions Cl2 play an important role in

Table 2. Selected bond lengths (nm) and angles (°) for complex 1

Complex 1			
Ni2–Cl1	0.2462(4)	Ni2–Cl1^{i}	0.2554(4)
Ni2–N1	0.2113(2)	Ni2–N2	0.2094(2)
Ni2–N3	0.2083(2)	Ni2–N4	0.2087(2)
N1–Ni2–N2	89.51(6)	N1–Ni2–N3	95.04(5)
N1–Ni2–N4	82.37(6)	N1–Ni2–Cl1	95.17(4)
N1–Ni2–Cl1i	175.36(4)	N2–Ni2–N3	83.14(5)
N2–Ni2–N4	171.12(5)	N2–Ni2–Cl1	93.12(4)
N2–Ni2–Cl1i	94.99(4)	N3–Ni2–N4	93.96(6)
N3–Ni2–Cl1	169.10(4)	N3–Ni2–Cl1^{i}	86.67(4)
N4–Ni2–Cl1	91.19(4)	N4–Ni2–Cl1^{i}	93.22(4)
Cl–Ni2–Cl1i	83.45(4)		

Symmetry code for complex 1: i, $-x$, $-y$, $-z$

the construction of the crystal structure. The 1D chain structure is hydrogen bonded between Cl2 anions and hydrogen atoms of amino groups of *en*-ligand to form a 3D supramolecular structure (Fig. 2b). Therefore, hydrogen bond interaction plays a very important role in the spatial configuration of the crystal material. The data on hydrogen bond lengths and bond angles are shown in Table 3.

In order to confirm the structural homogeneity of the bulk power materials, power X-ray diffraction (PXRD) experiment has been carried out. The PXRD experimental and computer-simulated patterns are in good agreement with each other (Fig. 3), indicating phase purity of complex 1.

Thermogravimetric analysis was used to determine the thermal stability. The weight loss in the range of 230 to 480°C is consistent with the removal of its four *en*-molecules (expt. 48.16, calcd. 48.19 %). According to the weight loss analysis, the final product may be $NiCl_2$ (expt. 51.85 %, calcd. 51.91 %) (Fig. 4).

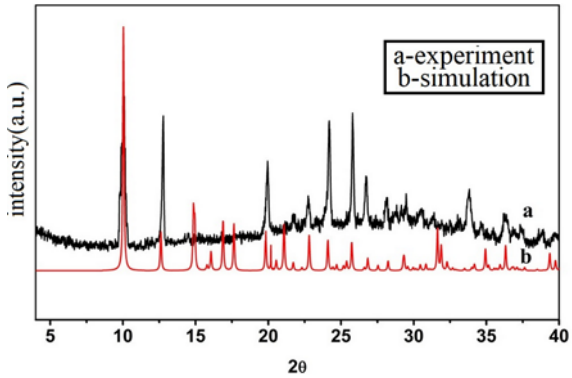

Fig. 3, The experimental (a) and simulative (b) powder X-ray diffraction patterns for complex 1.

Antibacterial activities were studied on Gram-negative Escherichia coli (E. coli) and Gram-positive Staphylococcus aureus (S. aureus), as shown in Fig. 5. It was found that filter papers with a blank, *en*-ligand and a low concentration of complex 1 had

Table 3. Hydrogen bond distances [nm] and angles [°] in complex 1

D–H	*d*(D–H)	*d*(H·A)	DDHA	*d*(D–A)	A
N3–H3A	0.09	0.278	135	0.3481(2)	Cl1^{ii}
N4–H4C	0.09	0.251	157	0.3358(2)	Cl1^{ii}
N1–H1A	0.09	0.260	167	0.3487(2)	Cl2^{iii}
N2–H2B	0.09	0.255	147	0.3346(2)	Cl2^{iv}
N3–H3B	0.09	0.233	173	0.3228(2)	Cl2^{v}
N4–H4D	0.09	0.266	147	0.3450(2)	Cl2^{vi}

Symmetry codes for complex 1: ii, $1 + x$, y, z; iii, $-0.5 + x$, $0.5-y$, $-0.5 + z$; iv, $-x$, $-y$, $1 - z$; v, $0.5 + x$, $0.5-y$, $-0.5 + z$; VI, x, y, $-1 + z$

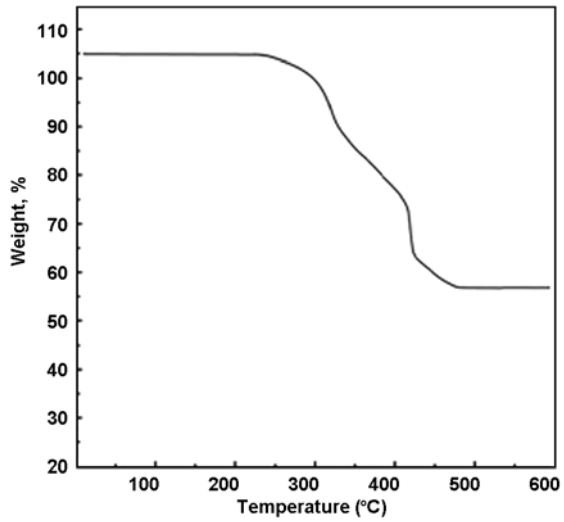

Fig. 4. TGA curve of complex 1.

no antibacterial activity against E. coli and S. aureus. With a gradual increase in the concentration, complex 1 showed excellent antibacterial activity against both E. coli and S. aureus. In addition, it can be seen from Fig. 5 that the antibacterial effect of complex 1 on Gram-negative bacteria is slightly better than that on Gram-positive bacteria. Comparison of the antibacterial activities of *en*-ligand with complex 1 of different concentrations showed that *en*-ligand had no antibacterial activities, and the antibacterial zone of the high concentration complex 1 was larger than the zone of complex 1 with a low concentration. These data show that the high concentration of the complex 1 has better antibacterial properties.

In order to further study and verify the antibacterial activities, the effect of complex 1 on the growth of E. coli was tested. The results showed that the growth curves of E. coli treated with 25, 50 and 100 μg/mL complex 1 were almost the same as those treated with free solvent without complex 1, showing a typical growth curve (Fig. 6). Therefore, it was shown that complex 1 at low mass concentration had no inhibitory effect on E. coli. OD_{600} of E. coli treated with 200, 400 and 800 μg/mL of complex 1 showed no obvious change at about 3–6 h compared with OD_{600} in the initial state, indicating that complex 1 had an inhibitory effect on the growth of E. coli. However, with increasing time, the growth trend of E. coli treated with 200 and 400 μg/mL complex 1 approached to the typical E. coli growth curve, indicating that the delay period of E. coli was prolonged compared to the low concentration. After 24 h of culture, the highest OD_{600} of E. coli treated with 200 and 400 μg/mL complex 1 was close to the control group at 0 μg/mL. That is, when E. coli reached a certain level, complex 1 with a mass concentration less than 400 μg/mL could no longer inhibit the growth of E. coli. Only complex 1 with a mass concentration 800 μg/mL could completely inhibit the proliferation and growth of E. coli in the culture medium within 24 h.

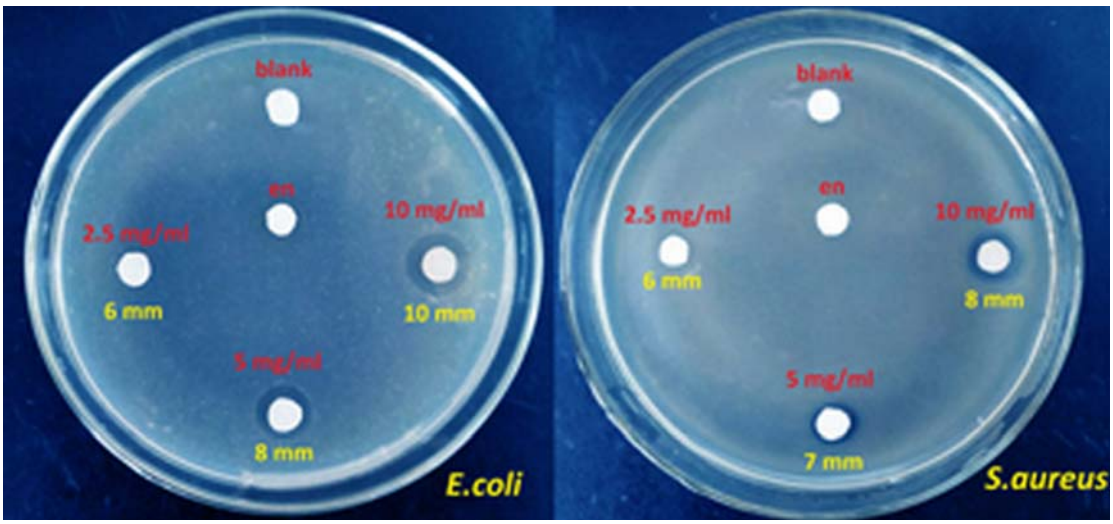

Fig. 5. Optical photograph of antibacterial tests of complex 1; left for negative E. coli and right for positive S. aureus.

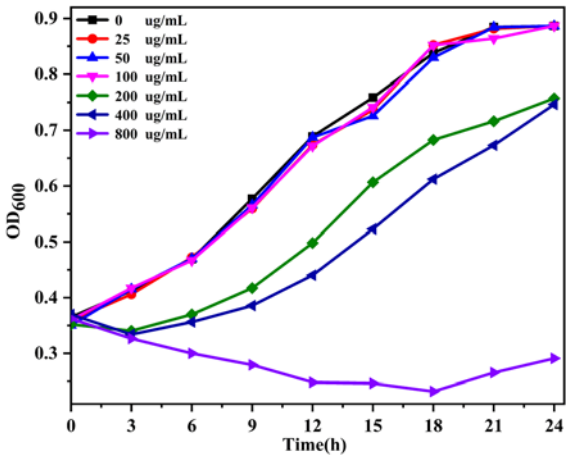

Fig. 6. Growth curves of E. coli at different concentrations of complex 1.

4. Conclusion

A complex, $[Ni_2(en)_4Cl_2]ClV2$ (1), with 0D structure was successfully synthesized by solvothermal method using interaction of en-ligand with Ni(II) ion, and a 3D supramolecular network structure was formed through N–H·Cl hydrogen bonds. The thermal stability of complex 1 was tested. The results show that the material of the crystal framework begins to collapse at about 230°C. In addition, antibacterial tests of complex 1 showed excellent antibacterial activities in the inhibitory region of Gram-negative bacteria, and complex 1 with mass concentration of 800 μg/mL could completely inhibit the proliferation and growth of E. coli in the culture medium within 24 h.

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