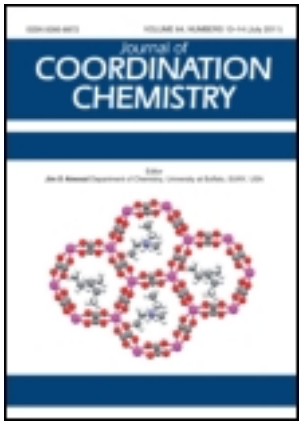

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Synthesis, crystal structure, and biological activity of 4′-chloro-2,2′:6′,2″-terpyridine (Cltpy) as tridentate ligand in a Cd(II) complex

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Synthesis, crystal structure, and biological activity of 4′-chloro-2,2′ : 6′,2″-terpyridine (Cltpy) as tridentate ligand in a Cd(II) complex

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A new Cd(II) complex with 4′-chloro-2,2′ : 6′,2″-terpyridine (Cltpy), $[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$, has been synthesized and characterized by CHN elemental analysis, ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy, and structurally analyzed by X-ray single-crystal diffraction. The single-crystal X-ray analyses show that the coordination number is seven with three terpyridine (Cltpy) N-donors, three oxygen atoms of two nitrates and one oxygen atom of methoxy/water. The antibacterial activities of Cltpy and its Cd(II) complex are tested against different bacteria. The free ligand has considerable activity against *Staphylococcus aureus*, *Bacillus anthracis*, and *Pseudomonas aeruginosa* (inhibition zones $\geq$ 20 mm), but has moderate activity against *Escherichia coli* and *Streptococcus pyogenes* (inhibition zones $\leq$ 15 mm). In comparison with free Cltpy ligand, its complex has more activity against *Klebsiella pneumonia*, *S. aureus*, and *B. anthracis* (inhibition zones $\geq$ 30 mm), but is inactive against *P. aeruginosa* and *S. pyogenes*. The quantitative assays gave minimal inhibitory concentration values in the range 6.25–100 mg mL^{-1} that confirmed the above results. Against *K. pneumonia* and *S. aureus*, antibacterial activity of the complex is higher than Cltpy ligand.

Keywords: Cd(II) complex; 4′-Chloro-2,2′ : 6′,2″-terpyridine (Cltpy); Synthesis; Crystal structure; Antibacterial properties

1. Introduction

Considerable attention has been drawn to metal complexes having 2,2′ : 6′,2″-terpyridine (tpy) or substituted tpy components due to their structural advantage in drug design and materials chemistry [1–7]. Syntheses of tpy derivatives have been extensively studied with varieties of substituted tpy compounds reported [8]. For example, they offered interesting prospects for metal-activated drug delivery, where the activity could be switched by metal–ion coordination through the study of the

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interactions between bioreceptors and a ligand with sugar substituents [8]. Besides the electrostatic interaction, non-covalent forces also play an important role in determination of the structural stacking and properties [9]. Interactions between aromatic rings are critical for molecular packing [10]; hydrogen bonds, powerful organizing forces in designing solids due to directionality, selectivity, and reversible formation at room temperature, may significantly influence the molecular packing in crystal engineering [11].

Pyridyl-based ligands such as 2,2′ : 6′,2″-terpyridine are commonly encountered due to structural and substituent versatility that is either commercially available or synthetically achievable. The 4′-position on terpyridine offers a broad range of substituents allowing variation of the inductive influence [12].

Coordination of 4′-chloro-2,2′ : 6′,2″ terpyridine (tpyCl) has been growing [12–20]. This ligand contains 2,2′ : 6′,2″-terpyridine (terpy) coordination site and another Cl site at the 4′-position, both sites are able to bind with different metal ions [17]. Terpy can bind to both low- and high-oxidation state metal ions, almost always tridentate [21–23].

In clinical applications and biochemistry, functionalized terpyridines have a wide range of potential uses, from colorimetric metal determination to DNA-binding agents [24]. Because of the binding to nucleic acids, metal terpyridine complexes have the potential to serve as anti-cancer, anti-bacterial, and anti-parasitic drugs [25, 26].

Cadmium appears as six-, seven-, or eight-coordinate; nitrates usually bond monodentate or bidentate [27, 28]. Group 12 ions exhibit complete nd shells, with no stabilizing ligand-field effects and geometries determined solely by size and electrostatic- or covalent-binding forces, allowing coordination diversity of any accompanying ligand. Cadmium complexes are more interesting from a structural point of view because of the ability to modify both coordination numbers and geometries [7, 29–31].

In this research we used new tridentate ligand 4′-chloro-2,2′ : 6′,2″-terpyridine (Cltpy) for synthesis of a new cadmium(II) complex. The structural and biological properties of the new complex have been studied.

2. Experimental

2.1. *Materials and measurements*

All chemicals were of reagent grade and used without purification. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer. FT-IR spectra were collected on a Shimadzu-IR Prestige 21 spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker spectrometer at 250 MHz in DMSO-d_6.

2.2. *Antibacterial activity test*

In vitro activity test was carried out using the growth inhibitory zone (well method) [32–34]. The potency of components was determined against three Gram-positive bacteria: *Streptococcus pyogenes* (RITCC 1940), *Staphylococcus aureus* (RITCC 1885), and *Bacillus anthracis* (RITCC 1036), and also against the three Gram-negative bacteria: *Klebsiella pneumonia* (RITCC 1249), *Escherichia coli* (RITCC 1330), and

Pseudomonas aeruginosa (RITCC 1547). Microorganisms (obtained from enrichment culture of the microorganisms in 1 mL Muller–Hinton broth incubated at 37°C for 12 h) were cultured on Muller–Hinton agar medium. The inhibitory activity was compared with that of standard antibiotics, such as gentamicin (10 μg). After drilling wells on the medium using a 6 mm cork borer, 100 μL of solution from different compounds were poured into each well. The plates were incubated at 37°C overnight. The diameter of the inhibition zone was measured as precisely as possible. Each test was carried out in triplicate and the average was calculated for inhibition zone diameters. A blank containing only methanol showed no inhibition in a preliminary test. The macro-dilution broth susceptibility assay was used for evaluation of minimal inhibitory concentration (MIC). The use of 12 test tubes is required by the macro-dilution method. By including 1 mL Muller–Hinton broth in each test, and then adding 1 mL extract with concentration 100 mg mL^{-1} in the first tube, we made a serial dilution of this extract from the first tube to the last tube. Bacterial suspensions were prepared to match the turbidity of 0.5 McFarland turbidity standards. Matching this turbidity provided bacterial inoculums of 1.5×10^8 cfu mL^{-1}. Then 1 mL of bacterial suspension was added to each test tube. After incubation at 37°C for 24 h, the last tube was determined as the MIC without turbidity.

2.3. *Preparation of [Cd(Cltpy)(NO$_3$)$_2$(H$_2$O)$_{0.45}$(CH$_3$OH)$_{0.55}$]*

4′-Chloro-2,2′ : 6′,2″-terpyridine (0.268 g, 1 mmol) was placed in one arm of a branched tube and cadmium(II) nitrate (0.165 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, the tube was then sealed and the ligand-containing arm immersed in a bath at 60°C while the other remained at ambient temperature. After 5 days, the crystals that had deposited in the cooler arm were filtered off, washed with acetone and ether, and air dried. Yield: 81%. Analysis: found (%): C: 35.84, H: 2.39, N: 13.10. Calcd for $C_{15.5}H_{13}CdClN_5O_7$ (%): C: 35.18, H: 2.47, N: 13.23. IR (cm^{-1}) selected bonds: 680(w), 819(m), 1005(m), 1040(m), 1292(s), 1385(vs), 1410(s), 1439(m), 1480(m), 1540(s), 1586(s), 2928(w), 3070(w). ^{1}H NMR (DMSO, δ): 7.770 (d, 2H), 8.211 (d, 2H), 8.701 (m, 4H), 8.916 (s, 2H), 3.405 (s, 3H) ppm. ^{13}C NMR (DMSO, δ): 123.35, 123.74, 127.53, 140.63, 140.96, 150.12, 156.35, 162.53, 39.94 ppm.

2.4. *X-ray crystallography*

2.4.1. Structure determination. Data collection for X-ray crystal structure determinations was performed on a STOE IPDS I/II diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data. The programs used in this work are Stoe's X-Area, including X-RED and X-Shape for data reduction and absorption correction, and the WinGX suite of programs, including Sir-92 and Shelxl-97 for structure solution and refinement [35]. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Materials for

publication were prepared using Mercury and ORTEP-3 [36, 37]. The summary of the crystal data, experimental details, and refinement results of the complex are listed in table 1.

3. Results and discussion

3.1. *Spectroscopic studies*

The reaction of Cadmium nitrate with 4′-chloro-2,2′ : 6′,2″-terpyridine (Cltpy) yielded crystalline material formulated as $[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$. IR spectra display characteristic absorption bands for tpyCl and for nitrate and methoxide. The relatively weak absorption bands at 3038–3100 and 2823–2951 cm^{-1} are due to C–H modes involving the aromatic ring and aliphatic hydrogen atoms, respectively. The absorption bands with variable intensity at 1400–1620 cm^{-1} correspond to aromatic ring vibrations of tpyCl. The characteristic vibration of methoxy stretching mode is at 1040 cm^{-1} (Supplementary material). The presence of bidentate and unidentate nitrate is associated with absorptions at 1245, 1292, 1385, 1496, and 1540 cm^{-1} [26, 27, 38].

Table 1. Crystallographic data of $[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$.

Identification code	$[Cd(terpy\text{-}Cl)\ (NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$
Empirical formula	$C_{15.5}H_{13}CdClN_5O_7$
Formula weight	529.16
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å,°)	
a	8.0002(12)
b	26.728(4)
c	10.0076(15)
α	90
β	106.009(3)
γ	90
Volume (Å^3), Z	2056.9(5), 4
Calculated density (g cm^{-3})	1.709
Absorption coefficient (mm^{-1})	1.239
$F(000)$	1048
Crystal size (mm^3)	$0.48 \times 0.32 \times 0.16$
θ range for data collection (°)	2.25–25.01
Index range	$-9 \le h \le 8$; $-24 \le k \le 31$; $-11 \le l \le 11$
Reflections collected	10,634
Independent reflections	3593
Absorption correction	Empirical
Max. and min. transmission	0.8263 and 0.5875
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3593/0/272
Goodness-of-fit on F^2	1.163
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0511$; $wR_2 = 0.1628$
R Indices (all data)	$R_1 = 0.0642$; $wR_2 = 0.1705$
Largest difference peak and hole (e Å^{-3})	1.611 and −0.519

The ^{1}H-NMR spectra of DMSO solutions of the complex at room temperature show two doublets, a singlet, and a multiplet for the aromatic protons of Cltpy. The singlet of $-CH_3$ of methanol is observed at 3.405 ppm (Supplementary material). The ^{13}C-NMR spectra of DMSO solutions show eight distinct bands assigned to aromatic carbon atoms of the pyridine rings of Cltpy; the signal for carbon of methanol appeared at 39.94 ppm.

3.2. *Structural analysis*

The solid-state structure was determined by single-crystal X-ray diffraction. Crystal and structure refinement data are given in table 1. X-ray crystal analysis reveals that the compound crystallizes in monoclinic with space group $P2(1)/c$. The crystal structure consists of 2-D layers that connect by hydrogen bonds. Each cadmium is chelated by three Cltpy nitrogen atoms, two oxygen atoms of bidentate nitrate, an oxygen atom of a monodentate nitrate, and methoxy (figure 1).

When CH_3OH was coordinated to Cd(II), the temperature factors of O and C were different. When trying to refine the structure with water coordinated instead of CH_3OH, residual electron density in the zone indicated that something more was there. Finally the structure refined supposing that Cd(II) is coordinated by CH_3OH (55%) or H_2O (45%). The precise formula of the complex now is $[Cd(C_{15}H_{10}N_3Cl)(NO_3)_2(CH_3OH)_{0.55}(H_2O)_{0.45}]$.

Cadmium(II) is in a slightly distorted pentagonal bipyramid. Selected bond lengths and angles are given in table 2. The Cd1–N1, Cd1–N2, and Cd1–N3 bond lengths of 2.345(5), 2.357(4), and 2.385(5) Å respectively, are within the normal range of Cd–N bonds. The bond lengths of Cd–O1N and Cd–O2N are 2.465(5) and 2.369(5) Å, respectively, showing the strain in bonding of bidentate nitrate.

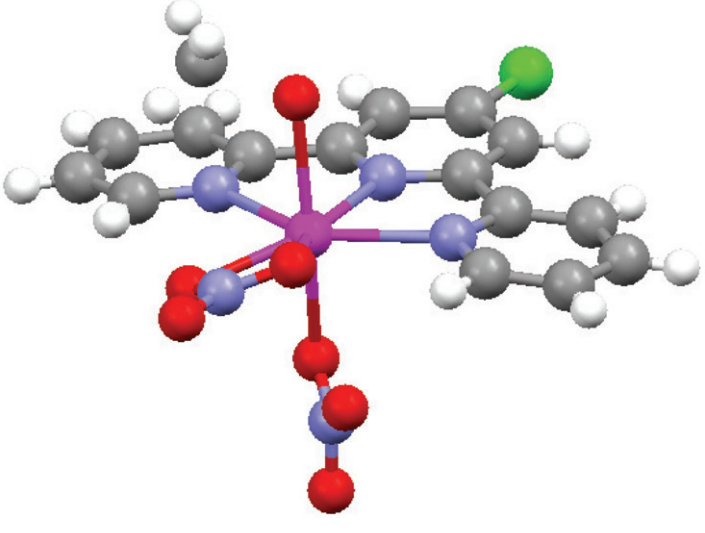

Figure 1. X-ray crystal structure of $[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$.

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

$[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$			
Cd1–N1	2.343(5)	N2–Cd1–O2N	154.8(2)
Cd1–N2	2.354(5)	N2–Cd1–O4N	82.9(2)
Cd1–N3	2.382(5)	N3–Cd1–O1N	134.1(2)
Cd1–O1N	2.467(6)	N3–Cd1–O2N	86.4(2)
Cd1–O2N	2.371(5)	N3–Cd1–O4N	83.9(2)
Cd1–O4N	2.378(9)	O1N–Cd1–O2N	52.7(2)
Cd1–O1W	2.389(8)	O1N–Cd1–O4N	111.6(2)
N1–Cd1–N2	69.2(2)	O1N–Cd1–O1W	77.6(2)
N1–Cd1–N3	138.3(2)	O2N–Cd1–O4N	89.0(2)
N1–Cd1–O1N	85.9(2)	O2N–Cd1–O1W	94.8(2)
N1–Cd1–O2N	135.0(2)	O4N–Cd1–O1W	170.4(2)
N1–Cd1–O4N	91.4(2)	N2–Cd1–O2N	154.8(2)
N1–Cd1–O1W	90.0(2)	N2–Cd1–O1N	151.9(2)

The N1N–O3N length [1.210 (8) Å] is 0.034 Å smaller than that of the N1N–O1N lengths [1.235(8) Å], or 0.066 Å smaller than that of the N1N–O2N lengths [1.276(8) Å]. All of these values show double bond character, but N1N–O3N has more double bond character. The cadmium nitrogen atoms angles are N1–Cd1–N2, 69.2(2)° and N2–Cd1–N3, 69.07(17)°, distorted from the pentagonal bipyramidal geometry (the angles must be 72°). The angles (°) of axial ligands to the equatorial plane are: N1–Cd1–O4N, 91.3(2); N2–Cd1–O4N, 82.8(2); N3–Cd1–O4N, 83.9(2); O1N–Cd1–O4N, 111.6(2); O2N–Cd1–O4N, 89.1(2); and N1–Cd1–O1S, 91.9(2); O1N–Cd1–O1S, 77.6(2); O2N–Cd1–O1S, 95.0(2) showing the distortion because of inter and intramolecular hydrogen bonds. The O4N–Cd1–O1S, 170.5(2) angle shows this distortion better. Views of unit cell and packing are shown in figure 2. Molecules occupy half of the tetrahedral holes and used zinc blend system that is not a close packed system. There are aromatic π–π stacking interactions between parallel aromatic rings of 4′-chloro-2,2′ : 6′,2″-terpyridine (Cltpy) as seen in figure 3. Intermolecular interactions in crystals of $[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$ are shown in table 3 and figure 4. Figure S3 (Supplementary material) shows the powder X-ray diffraction patterns of the complex with sharp pattern and no amorphous phases.

3.3. *Antibacterial activity*

The antibacterial activities of Cltpy and its Cd(II) complex are shown in table 4. The free ligand has considerable activity against *S. pyogenes*, *B. anthracis*, and *P. aeruginosa* (inhibition zones $\geq$20 mm), and moderate activity against *E. Coli* and *S. aureus* (inhibition zones $\leq$15 mm) [32]. In comparison with free Cltpy, the complex has strong activity against *K. pneumonia*, *S. aureus* and *B. anthracis* (inhibition zones $\geq$30 mm), but is inactive against *P. aeruginosa* and *S. pyogenes* [33, 34].

MIC is the lowest concentration of an antimicrobial agent that will inhibit visible growth of a microorganism after incubation and its amount shows resistance of microorganisms to an antimicrobial agent. MIC amounts are 6.25–100 mg mL^{-1}.

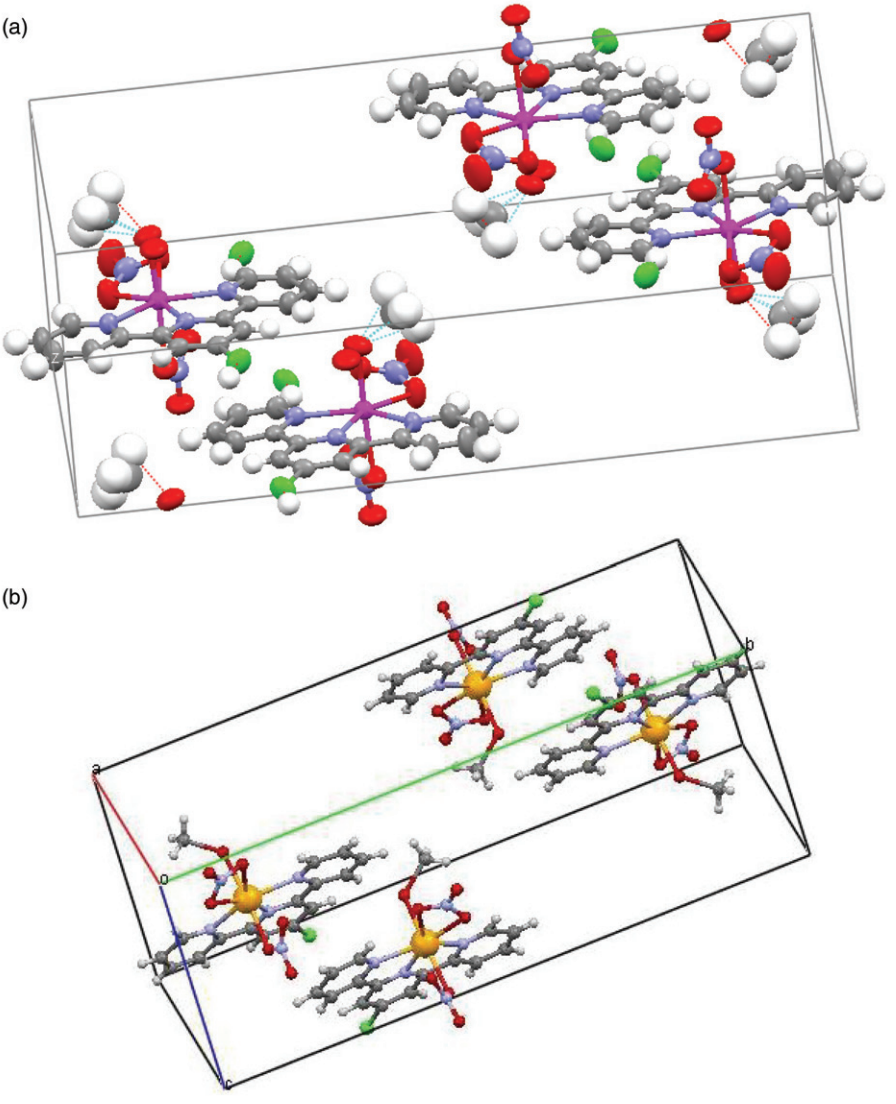

Figure 2. Two views of the unit cell.

Growth inhibition zone and MIC have reverse relation, when the growth inhibition zone is increased the value of MIC is decreased, as seen in table 4.

It should be noticed that the MIC(mg mL^{-1}) of Cltpy ligand is lower than standard antibiotic (gentamicin) against *S. pyogenes* and *B. anthracis*.

Against *K. pneumonia* and *S. aureus*, antibacterial activity of the complex is higher than that of Cltpy. The higher activity of the complex may be explained on the basis of chelation theory [32] and existence of NO_3^- in its structure [33, 34]. The quantitative assays gave MIC values in the range 6.25–100 mg mL^{-1} (table 4).

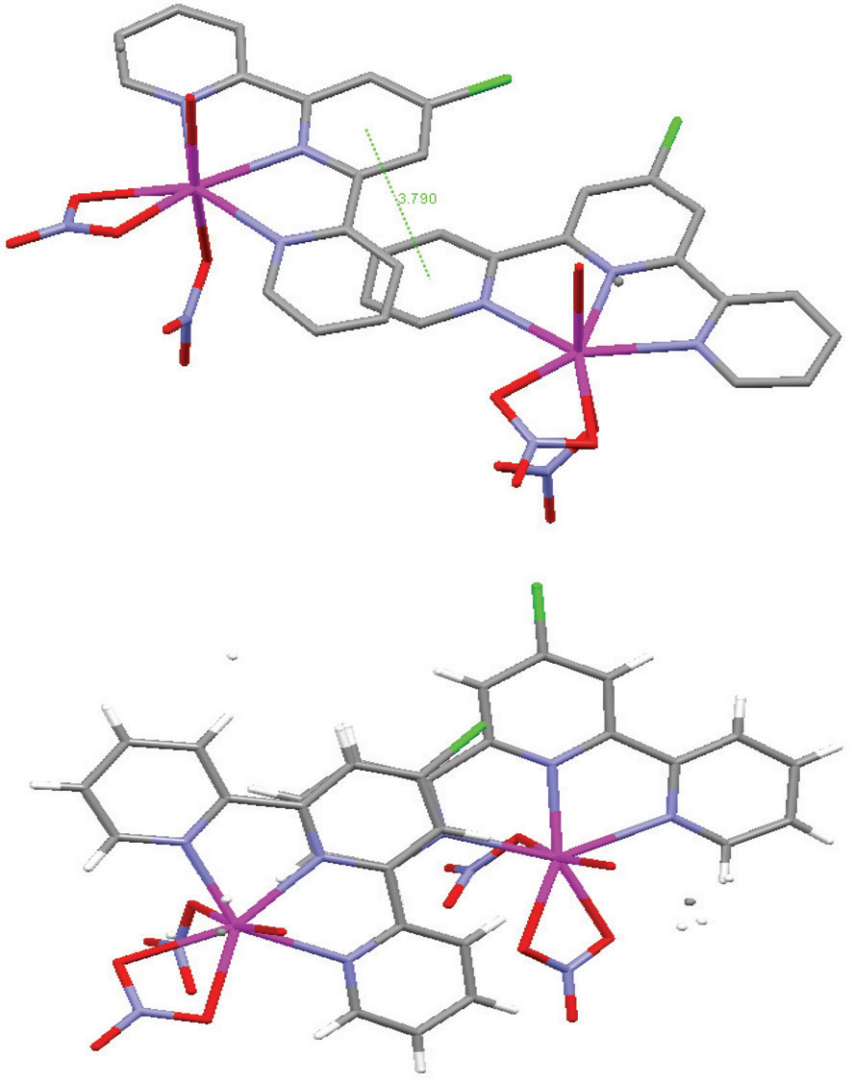

Figure 3. Two views of π–π stacking interactions between parallel aromatic groups.

Table 3. Intermolecular interactions in crystals of $[Cd(Cltpy)(NO_3)_2](H_2O)_{0.45}(CH_3OH)_{0.55}$.

A···H–B	H···A(Å)	B···A(Å)	B–H···A( )
O3N···H9–C9 ($-x$, y, $-z+1/2$)	2.713	3.623(2)	166.13
O3N···H12–C12 ($-x$, y, $-z+1/2$)	2.541	3.434(2)	161.13
O4N···H2–C2 ($-x$, y, $-z+1/2$)	2.591	3.317(2)	135.32
Cl1···H1–C1	2.715	3.478(2)	139.71
O6N···H13 ($-x$, y, $-z+1/2$)	2.815	3.594(2)	141.95
O1W···H4 ($-x$, y, $-z+1/2$)	2.753	3.657(2)	163.93
O6N···C10		3.045	
O6N···O1S ($-x$, y, $-z+1/2$)		2.799	
O5N···O1N		2.996	
Centroid···centroid (N1C1–C5)···(N2C6–C10)		3.791	

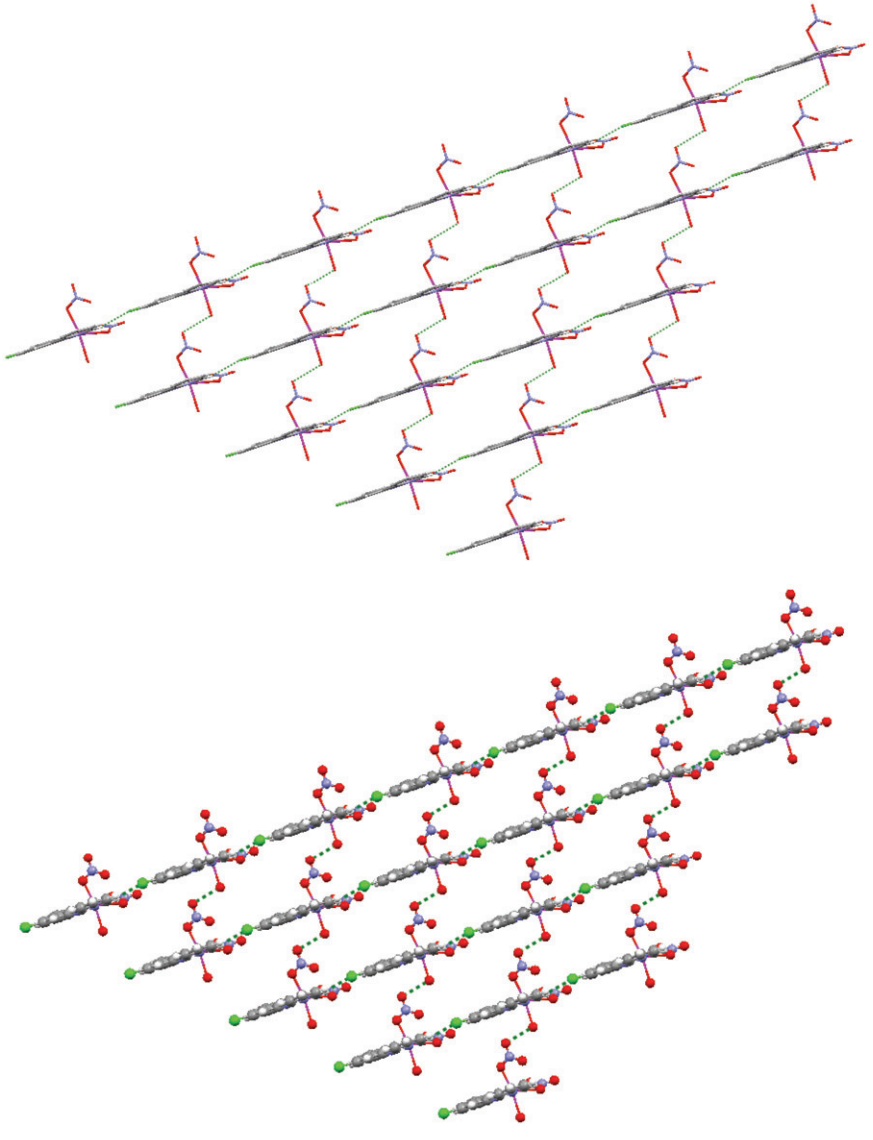

Figure 4. Two views of layered packing structure.

Table 4. Antibacterial activities (zone of growth inhibition and MICs) of Cltpy ligand and Cd(II) complex and gentamicin (as a standard compound).

		Microorganisms					
Method	Main compounds	*K. pneumonia* (−)	*E. coli* (−)	*P. aeruginosa* (−)	*S. pyogenes* (+)	*B. anthracis* (+)	*S. aureus* (+)
Growth inhibitory zone (mm)	Cltpy	10	15	20	30	25	15
	Complex	35	20	–	–	30	30
Standard	Gentamicin	20	25	15	13	32	20
MIC ($mg\,mL^{-1}$)	L	100	100	50	6.25	12.5	100
	Complex	6.25	50	–	–	6.25	6.25

4. Conclusion

New tridentate 4′-chloro-2,2′ : 6′,2″-terpyridine (Cltpy) has been used to prepare $[Cd(Cltpy)(NO_3)_2(H_2O)_{0.45}(CH_3OH)_{0.55}]$, characterized by CHN elemental analysis, ^{1}H-NMR, ^{13}C-NMR, IR spectroscopies, and structurally analyzed by X-ray single-crystal diffraction. The coordination number is seven with three terpyridine (Cltpy) N-donor atoms, three nitrate oxygen atoms, and one methoxy. The antibacterial activities of Cltpy and its Cd(II) complex are tested against different bacteria. Against *K. pneumonia* and *S. aureus*, antibacterial activity of the complex is higher than free Cltpy and gentamicin.

Comparison of the biological activity of this newly synthesized complex with the reported activities of other Cd(II) complexes shows there is a fairly good relationship among the reported results and in some cases the activity of this complex is better than previous complexes [39–41].

The study on structure–activity relationship of these compounds indicated that the hydrophilicity and aromaticity seemed to be important for antibacterial activity [42]. With the increase of hydrophilicity and aromaticity of the compounds, the activity of compounds increased. The presence of nitrate and high stability of the formed complex may be helpful in the activity.

Supplementary material

CCDC reference number 799986 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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