Scientific paper

Synthesis, Characterization, Crystal Structure, and Biological Studies of Two New Cd (II) Complexes with 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine (Clphtpy)

Lotfali Saghatforoush,[1,*] Hadi Amiri Rudbari,[2] Francesco Nicolò,[3] Parvin Asgari,[1] Firoozeh Chalabian,[4] Mohammad Hasanzadeh[5] and Vahid Panahiazar[5]

[1] *Department of Chemistry, Payame Noor University, 19395-4697, Tehran, I.R. of Iran*

[2] *Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran*

[3] *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone, 31 Contrada Papardo, 98166 Messina, Italy*

[4] *Department of Biology, Islamic Azad University, Tehran North Campus, Tehran, Iran*

[5] *Drug applied Research Center, Tabriz University of Medical Sciences, Tabriz 51664, Iran*

** Corresponding author: E-mail: saghatforoush@gmail.com*
Tel: +98 4612349868, fax: +98 4612332556

Received: 14-11-2012

Abstract

Two new Cd(II) complexes, with the ligand 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine (Clphtpy) formulated as: $[Cd(Clphtpy)(NO_3)_2H_2O]$ (**1**), and $[Cd(Clphtpy)(N_3)_2]_2$ (**2**), have been synthesized and characterized by CHN elemental analysis as well as FT-IR, ^1H NMR, absorption and emission spectroscopy, thermal analysis and analyzed structurally by X-ray single-crystal diffraction. The single crystal X-ray analysis showed that the coordination number in complex **1** and **2** were seven and six with N_3O_4 and N_6 coordination sphere, respectively. The antibacterial activities of the synthesized complexes were tested against four gram-positive and four gram-negative bacteria. A biological study of the complexes indicated that the complex **1** exhibited very good activity against most of the tested bacteria and its activity was better than gentamicin as a standard antibiotic.

Keywords: Cd(II) complexes; 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine (Clphtpy); Synthesis; Crystal structure; antibacterial properties

1. Introduction

Polypyridyl compounds have ring nitrogen atoms serving as multiple interactions sites, and form stable coordination complexes with various metal ions.[1] The interactions among the aromatic rings are found to be critical for the molecular packing in crystallization.[2] In recent years, considerable attention has been drawn to the family of metal complexes having 2,2':6',2''-terpyridine (tpy) or substituted tpy components due to their structural advantage in drug design, material chemistry and photofunctional supramolecular assemblies.[3] Compared with 2,2':6',2''-terpyridine (tpy), 4'-chlorophenyl 2,2':6',2''-terpyridine (L) has an additional hydrogen-bond acceptor which makes formation of N–H···Cl and C–H···Cl hydrogen bonds possible.[4] Furthermore, the hydrogen bond, a powerful organizing force in designing solids due to its directionality, selectivity and reversible formation at room temperature, may significantly influence the molecular packing in the crystal engineering. It is reasonable to predict that the cadmium compounds on Clphtpy and appropriate linkers, such as halide and pseudo-halide X (Cl, Br, I, SCN or CN), can be developed from monomers to polymers.[5]

Recently, the design and construction of inorganic–organic hybrid materials, containing group XII metal ions such as Cd^{2+}, have attracted considerable attention

for their special functional properties such as optics, separation and catalysis, as well as the variety of architectures and topologies.[6] We have newly reported structural characterization of Cd(II) complexes of Cltpy[7–8] and Mephtpy[9] ligands. In this study we report the preparation, structural characterization and comparison of two cadmium(II) complexes with two different counter ions with the formula of $[Cd(Clphtpy)(NO_3)_2H_2O]$, **1**, and $[Cd(Clphtpy)(N_3)_2]_2$, **2**, respectively and the antibacterial activity of both terpyridine based cadmium complexes against four gram-positive and four gram-negative as well as their thermal properties.

2. Experimental

2. 1. Reagents and Instrumentation

4'-(4-chlorophenyl)-2,2':6',2''-terpyridine is commercially available from Aldrich and is used without any changes. All other solvents and chemicals were of reagent grade and used without further purification. Elemental analyses (CHN) were performed using a Perkin-Elmer model 2400 II analyzer. FT-IR spectra were collected on a Shimadzu-IR Prestige 21 spectrophotometer in the range of 4000–400 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded with a Bruker spectrometer at 250 MHz in D_6-DMSO. TGA were obtained on a Mettler-Toledo TGA 851e at a heating rate of 10 °C min^{-1} in air. Measurements of the luminescence spectra and intensity were carried out using a JASCO FP-750 spectrofluorometer (Tokyo, Japan) equipped with a 150-W Xenon lamp and 1.0 cm quartz cells. The excitation and emission monochromator bandwidths were 10 nm. All measurements were carried out at 25 °C, using a Peltier thermostated cell holder (Tokyo, Japan).

2. 2. Antibacterial Activity Test

The bacterial species in this study involve: four Gram-positive bacteria: *Staphylococcus epidermidis* (RTCC 1898), *Streptococcus B agalactiae* (RTCC 1913), *Listeria monocytogenes* (RTCC 1293) and *Bacillus cereus* (RTCC 1040) and also four Gram-negative bacteria: *Enterobacteraerogenes* (RTCC 1145), *Klebsiellapneumoniae* (RTCC 1249), *Pseudomonas aeruginosa* (RTCC 1547) and *Escheichia coli* (RTCC 1330). The inhibition effect on bacteria growth was determined by disc diffusion method.[10–13] Each compound was dissolved in DMSO as a solvent (1g/10 ml) and 30 µl of each solution applied on the paper disc (the disc diameter was 6 mm). The impregnated discs with different solutions were left for complete evaporation of the solvent. Then disc papers were placed on the inoculated plates with the bacteria of interest. After incubation in the standard upside down position in 35 °C for 24 h, zones of growth inhibition around each of the discs were measured to the nearest millimetre. A blank, containing only DMSO, showed no inhibition in a preliminary test. The macrodilution broth susceptibility assay was used for the evaluation of minimal inhibitory concentration (MIC).[11]

2. 3. Synthesis of Cd(II) Complexes

2. 3. 1. Preparation of $[Cd(Clphtpy)(NO_3)_2H_2O]$ (1)

4'-(4-chlorophenyl)-2,2':6',2''-terpyridine (0.172 g, 0.5 mmol) and cadmium(II) nitrate (0.154 g, 0.5 mmol) were placed in the main arm of a branched tube**.** Methanol was carefully added to fill both arms. The tube was then sealed and the main arm was immersed in a bath at 60 °C while the other remained at ambient temperature. After two days, the crystals that had been deposited in the cooler arm were filtered off, washed with diethylether, and dried in the air. Yield: 75%. Analysis: found: C: 42.02, H: 2.55, N: 11.44%. Calculated for $C_{21}H_{16}CdClN_5O_7$: C: 42.16, H: 2.69, N: 11.70%. **IR** (cm^{-1}) selected bands: 1384(m), 1423(m), 1496(s), 1540(bs), 1600(s), 2993(w), 3082(m).**^{1}H NMR** (250 MHz, DMSO, δ): 7.69 (d, 2H), 7.72 (t, 2H), 8.19 (t, 2H), 8.23 (d, 2H), 8.77 (d, 2H), 8.85 (d, 2H), 8.90 (s, 2H) ppm.

2. 3. 2. Preparation of $[Cd(Clphtpy)(N_3)_2]_2$ (2)

4'-(4-chlorophenyl)-2,2':6',2''-terpyridine (0.172 g, 0.5 mmol), cadmium(II) acetate (0.132 g, 0.5 mmol) and sodium azide (0.064 g, 1 mmol) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was then sealed and the main arm was immersed in a bath at 60 °C while the other remained at ambient temperature. After two days, the crystals that had been deposited in the cooler arm were filtered off, washed with diethylether, and dried in the air. Yield: 80%. Analysis: found: C: 46.42, H: 2.46, N: 23.18%. Calculated for $C_{42}H_{28}Cd_2Cl_2N_{18}$: C: 46.68, H: 2.61, N: 23.33%. **IR** (cm^{-1}) selected bands: 1604(s), 2032(s), 2058(s), 2997(w), 3066(m). **^{1}H NMR** (DMSO, δ): 7.69 (d, 2H), 7.70 (t, 2H), 8.21 (t, 2H), 8.29 (d, 2H), 8.75 (d, 2H), 8.85 (d, 2H), 8.90 (s, 2H) ppm.

2. 4. X-Ray Crystallography

2. 4. 1. Structure Determination

X-ray data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo K_α radiation (λ = 0.71073 Å). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with Bruker software.[14] The structures were solved by direct methods using SIR2004.[15]

The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL.[16] All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

3. Results and Discussion

3. 1. Spectroscopic Studies

The reaction of 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine with Cadmium salts (nitrate and acetate) and sodium azide as a counter ion in methanol gave colorless solids of empirical formulation $[Cd(Clphtpy)(NO_3)_2H_2O]$ **(1)** and $[Cd(Clphtpy)(N_3)_2]_2$ **(2)**.

The IR spectra display characteristic absorption bands for the Clphtpy ligand and for the azide anion. The relatively weak absorption bands at around 3032–3100 cm^{-1} are due to the C-H modes involving the aromatic rings. The absorption bands with variable intensity in the frequency range 1400–1600 cm^{-1} correspond to aromatic ring vibrations of the Clphtpy ligand. In complex **2**, $\nu_{as}(N_3)$ appears as a very strong splitting band at 2032 and 2058 cm^{-1} is assigned to the existence of end-on bridging azide ligand.[17–19] The presence of coordinated nitrate in **1** is associated with absorptions at 1384 cm^{-1}.[20–22] The ^1H NMR spectra of complexes were recorded in DMSO-d6 solution. The signals for aromatic protons of the terpyridine rings of both complexes appear in the region δ 7.67–9.07. Four doublets in the range 7.69, 8.23–8.29, 8.77–8.75, 8.85 ppm region, two triplets in the 7.67–7.71 and 8.18–8.21 ppm regions and one singlet in the range 8.90 ppm region for the aromatic protons of Clphtpy observed.

3. 2. Structural Analysis

The solid state structure of compounds **1** and **2** were determined by single crystal X-ray diffraction. Crystal and structure refinement data of the two compounds are given in Table 1. Selected bond lengths and angels of **1** and **2** complexes are given in Table 2.

3. 2. 1. Crystal Structure of $[Cd(Clphtpy)(NO_3)_2H_2O]$ (1)

An X-ray diffraction study of **1** reveals that it packs into the Monoclinic with space group P2(1)/c. The crystal structure of complex **1** consists of a monomeric unit of $[Cd(Clphtpy)(NO_3)_2(H_2O)]$. Each cadmium atom chelated by three Clphtpy nitrogen atoms, two oxygen atoms of bidentate nitrate, an oxygen atom of a monodentate nitrate, and water. The resulting coordination number of seven is augmented with CdN_3O_4 molecule core (Fig. 1).

The cadmium(II) atom has a distorted pentagonal bipyramid where the equatorial positions are occupied by

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	Complex 1	Complex 2
Empirical formula	$C_{21}H_{16}CdClN_5O_7$	$C_{42}H_{28}Cd_2Cl_2N_{18}$
Formula weight	598.24	1080.52
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
Unit cell dimensions	a = 7.5832(5) Å	a = 16.9389(4) Å
	b = 19.7841(13) Å	b = 13.9881(4) Å
	c = 15.0525(9) Å	c = 19.4737(5) Å
	α = 90°	α = 90°
	β = 90.871(4)°	β = 103.7380(10)°
	γ = 90°	γ = 90°
Volume	2258.0(2) $Å^3$	4482.2(2) $Å^3$
Z	4	4
Density (calculated)	1.760 g cm^{-3}	1.601 g cm^{-3}
Absorption coefficient	1.140 mm^{-1}	1.122 mm^{-1}
F (000)	1192	2144
Crystal size	0.24 × 0.17 × 0.15 mm^3	0.26 × 0.16 × 0.15 mm^3
Theta range for data collection	2.69 to 28.09°	2.33 to 28.00°
Index ranges	–10≤ h ≤ 10	–22≤ h ≤ 22
	–26≤ k ≤ 26	–18≤ k ≤ 18
	–19≤ l ≤ 19	–25≤ l ≤ 25
Reflections collected	72280	67516
Data / restraints / parameters	5465 / 2 / 324	10803 / 0 / 585
Goodness-of -fit on F^2	1.130	0.865
Final *R* indices [I>2σ(*I*)]	R1 = 0.0379	R_1= 0.0335
	wR2 = 0.0778	wR_2= 0.0993
R Indices (all data)	R1 = 0.0571	R_1= 0.0545
	wR2 = 0.0903	wR_2= 0.1261
Largest diff. Peak, hole	0.464 and –0.420 e.$Å^{-3}$	0.820 and –0.542 e.$Å^{-3}$

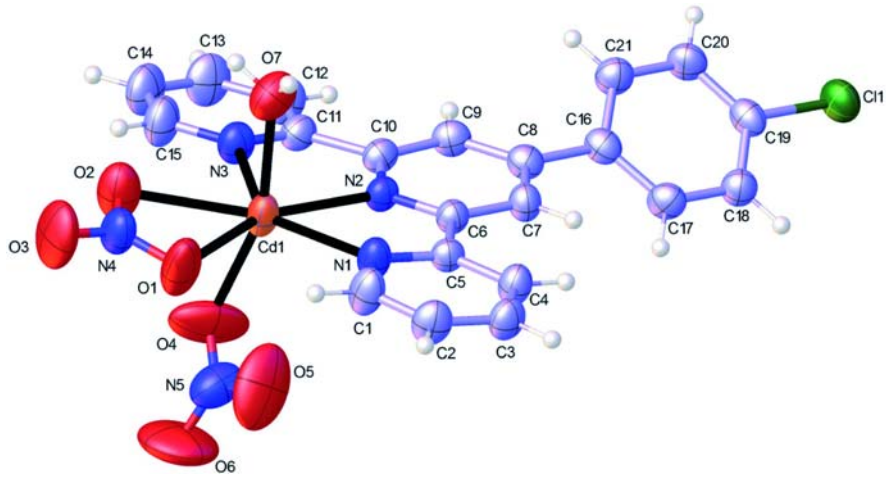


Fig. 1. Molecular structure of **1** including the atom numbering scheme

a tridentate terpyridine and a bidentate anion, NO_3^-. The remaining two apical positions are occupied by one monodentate nitrate and water. The terpyridine unit is not planar (interannular torsion angles: 8.55°, 5.74°). In most cases, due to the resonance stabilization through the whole molecule the coplanar structure is favored for three pyridine rings of 4'-(4-chlorophenyl)-2,2':6',2''-terpyridine, and this coplanar structure can be further stabilized by the formation of coordinative bonds between the terpyridine system and the metal ions.[2] The central pyridine ring of **1** forms a dihedral angle of 5.74° with the plane (N1C1–C5) and an angle of 8.55° with the other plane (N3C11–C15), showing that the three connected planes are slightly far from coplanarity. On the other hand, the pendent chlorophenyl, has rotated and formed a dihedral angle with the central pyridyl ring of 34.37°. The observed distortion is believed to be for the presence of C–H···X hydrogen bonding interaction. The Cd-N bond lengths are within the normal range bonds.[7–9] The bond lengths of cadmium-oxygen$_{nitrate}$ (Cd–O1 and Cd–O2) show the strain in bonding of bidentate nitrate. The angles of N1-Cd-N2 and N2-Cd-N3 are distorted from the pentagonal bipyramidal geometry (the angles must be 72°). Views of unit cell and packing are shown in Fig. 2.

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

Complex 1		**Complex 2**	
Cd1–N1	2.349(3)	Cd1–N2	2.305(2)
Cd1–N2	2.320(2)	Cd1–N3	2.400(3)
Cd1–N3	2.359(3)	Cd1–N4	2.257(3)
Cd1–O1	2.437(3)	Cd1–N5	2.282(3)
Cd1–O2	2.446(3)	Cd(1)–N(5)#1	2.453(3)
Cd1–O4	2.509(5)	Cd2–N10	2.363(2)
Cd1–O7	2.377(4)	Cd2–N11	2.309(2)
		Cd2–N12	2.370(3)
N1–Cd1–N2	69.75(9)	Cd2–N13	2.486(4)
N2–Cd1–N3	69.74(9)	Cd2–N13#2	2.258(3)
N1–Cd1–O4	113.27(14)	Cd2–N14	2.274(6)
N2–Cd1–O4	95.28(17)		
N3–Cd1–O4	76.62(13)	N1–Cd1–N2	70.06(9)
O1–Cd1–O4	91.47(17)	N2–Cd1–N3	69.72(8)
O2–Cd1–O4	83.72(18)	N4–Cd1–N3	94.83(11)
N1–Cd1–O7	83.77(11)	N4–Cd1–N5	91.33(11)
O1–Cd1–O7	84.51(13)	N4–Cd1–N1	96.18(12)
O2–Cd1–O7	80.17(12)	N4–Cd1–N5#1	158.67(10)
O4–Cd1–O7	162.16(16)	N10–Cd2–N11	70.27(9)
		N11–Cd2–N12	69.63(10)
		N14–Cd2–N10	100.70(18)
		N14–Cd2–N12	89.61(18)
		N13–Cd2–N10	95.20(13)
		N13–Cd2–N12	81.82(13)
		N13#2–Cd2–N13	74.49(13)
		N13–Cd2–N14	163.07

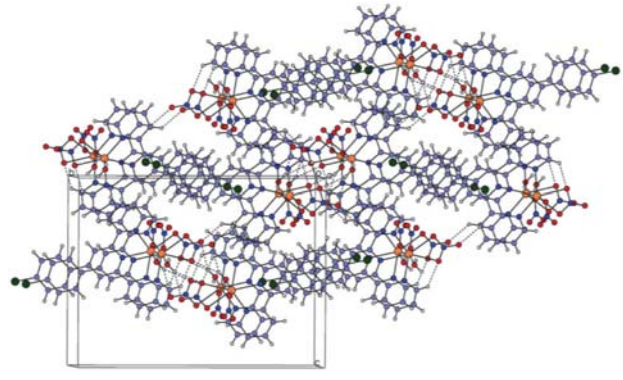


Fig. 2. Packing of **1** to form 3D supramolecularlayers through intermolecular and intramolecular interactions

Weak intermolecular π–π stacking is found among terminal pyridine rings with the shortest contact of 3.958 Å (Fig. 3a). Weak C-H···Cl hydrogen bonding interactions are also found between the pyridine protons and Cl^- an-

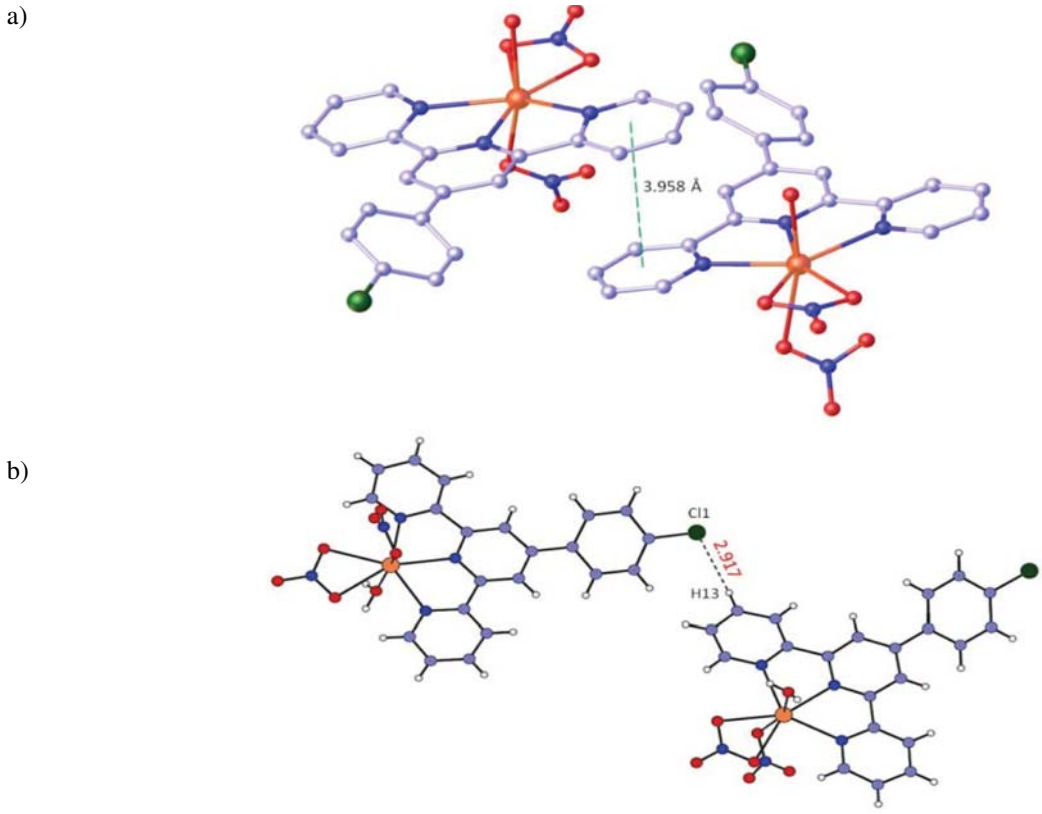


Fig. 3. (a) View of π–π stacking interactions between parallel aromatic rings of complex **1**. (b) Hydrogen bonding ineractions between the pyridine protons and Cl^- anions

ions (Fig 3b and Table 3). Specific short contacts between certain hydrogens of the terminal pyridine ring, water and oxygen of certain NO_3^- ligands (O9···H4, O9···H3, O6···H1 and O4···HW) assist to the building up a 3D framework (Fig. 2).

3. 2. 2. Crystal structure of $[Cd(Clphtpy)(N_3)_2]_2$ (2)

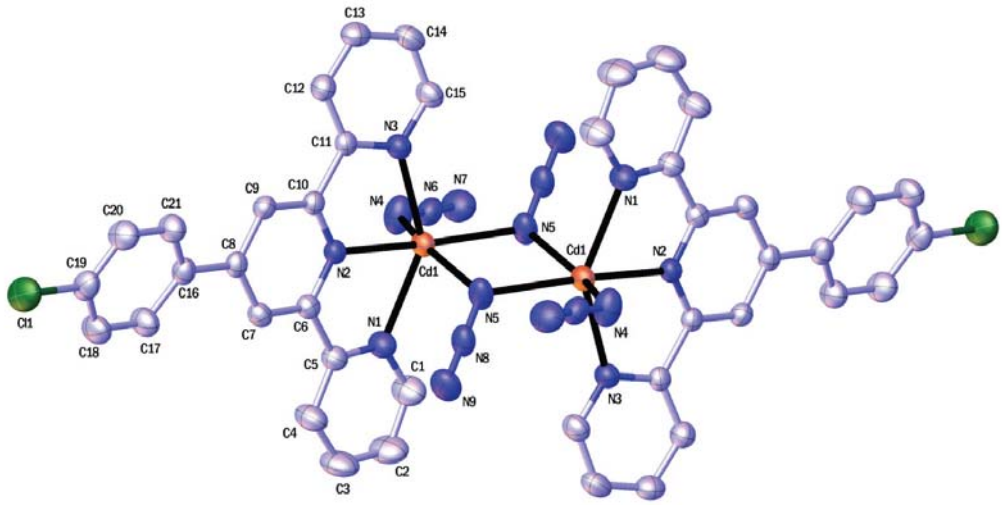
The complex **2** was shown by single crystal X-ray diffraction to be crystallized in the monoclinic with space group P2(1)/c. Determination of the structure by X-ray crystallography shows that the asymmetric unit of **2** comprises two independent binuclear cadmium complexes with the same coordination environment, $Cd1N_6$ (**2A**) and $Cd2N_6$ (**2B**). Selected bond lengths and angels of **2** are given in Table 2.

The crystal structure of **2** exhibits two discrete dimers in the solid state with $Cd(\mu\text{-}N_3)_2Cd$ type bridging. Each cadmium atom chelated by three Clphtpy nitrogen atoms, a terminal and two bridging nitrogen atoms of azide (Fig 4a). The Cd1···Cd1 and Cd2···Cd2 separations are 3.821 Å and 3.779 Å, respectively. The three aromatic rings of the Clphtpy ligand are not coplanar; the biggest dihedral angles are 10.67° and 7.47° for **2A** and **2B**, respectively. The pendent Clphenyl has rotated and formed a dihedral angle with the central pyridyl ring of 19.43° and 15.18° for **2A** and **2B**, respectively that shows twisted angle of Clphenyl substituent in **1** is higher than **2A** and **2B**.

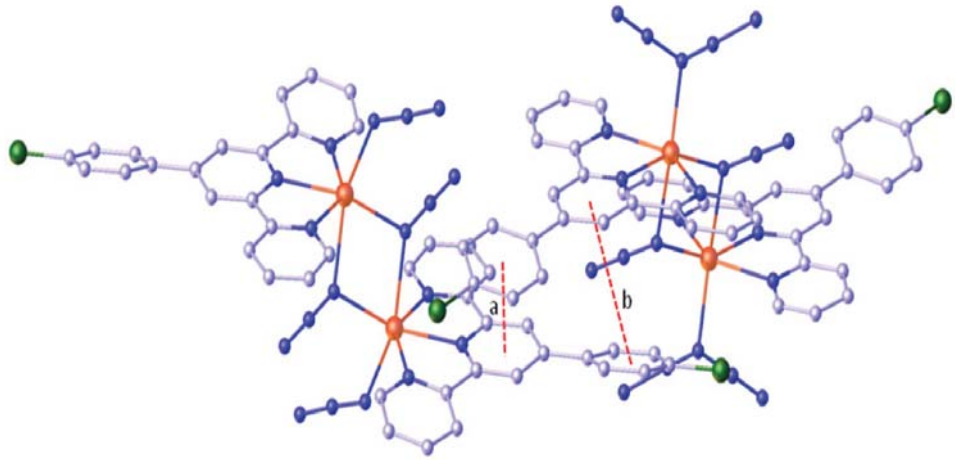
Similar to complex **1**, Intermolecular and intramolecular hydrogen bondings and π–π stacking interactions are observed in **2**, and seem to be responsible for the arrangement of complexes in the crystal packing. An inspection of **2** for weak directional intermolecular interactions by the program MERCURY, which were used for calculating the supramolecular interactions, shows that there are C-H···N_{azide} and C-H···Cl interactions (Table 3) (Fig. 4b-4c). The C-H···N_{azide} separations range from 2.408 to 2.695 Å (Table 3), which is indicative of moderate-to strong hydrogen bonds.[23] This cooperativity between the C-H···anion interactions obviously enhances the bonding association and the anion binding properties of the system. The terpyridine molecules are parallel in the crystal packing, forming a layer packing structure with an interlayer distance of 3.48 Å. The centroid to centroid separations between neighboring aromatic rings exhibit typical π–π stacking interactions in a face to face fashion. Thus, a three-dimensional hydrogen-bonded and layer-packed network is constructed.

The comparison of obtained dihedral angles shows that the three connected planes are far from coplanarity in **2A** respects to **1** and **2B**.

a)



b)



c)

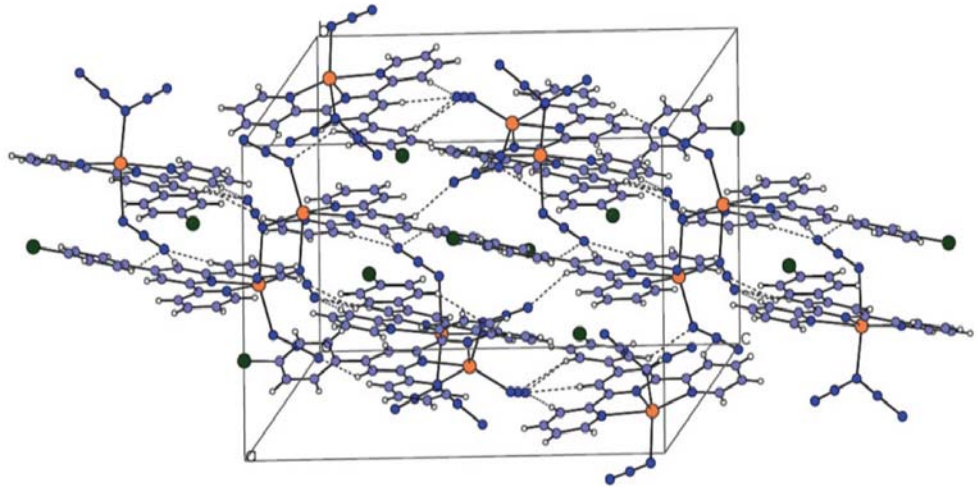


Fig. 4. (a) Molecular structure of **2** including the atom numbering scheme. The asymmetric unit contains half of two independent molecules. Only one dimer has been shown for clarity. Also, hydrogen atoms have been emitted for clarity (b) Intermolucular face-to-face π–π stacking of two discrete dimer of **2** [Attention: the azide group of one molecule in the asymmetric unit cell is disordered over two positions in a 80:20 ratio] (c) Packing diagram od **2** with inermolecular interactions shown as dotted lines.

Table 3. Intermolecular interactions in crystals of **1** and **2**.

B···H–A	B···H	B···A	<B···H–A
Complex 1			
[a] Cl1···H13C13	2.917	3.837	169.94
O6···H1C1	2.612	3.096	113.03
[b] O4···HW	2.346	3.156	171.62
O9···H3C3	2.514	3.065	118.17
O9···H4C4	2.388	3.006	123.77
Complex 2			
[c] Cl1···H39C39	2.975	3.875	165.47
[d] N7···H9C9	2.442	3.238	143.74
N7···H12C12	2.695	3.591	161.94
N16···H4C4	2.490	3.415	173.91
N16···H7C7	2.549	3.479	177.39
[e] N15···H17C17	2.681	3.301	124.76
[e] N16···H17C17	2.542	3.349	145.23
[f] N9···H33C33	2.408	3.335	174.63
N9···H30C30	2.582	3.512	176.74
N9···H42C42	2.619	3.478	153.67
[h] N8···H42C42	2.607	3.317	133.55

[a] (–2–x,1/2+y,1.5–z), [b] (1+x,y,z), [c] (1–x,–y,2–z), [d] (1–x,–1/2+y,1/2–z), [e] 1–x,–y,1–z), [f] (2–x,–y,2–z), [h] (x,y,z)

Comparison of these structures with the reported structures,[9] indicates deviation from coplanarity of terpyridine rings in complexes derived from Clphtpy which is higher than Mephtpy significantly (probably due to weak Cl···H hydrogen bonding). Also this comparison discloses that methyl derivation with Cl^- doesn't create any considerable changes in Cd(II) coordination mode but it leads to the considerable changes in crystal structure packing.[9]

4. Antibacterial Activity

The antibacterial activities of Clphtpy and its Cd(II) complexes are shown in Table 4. Although antibacterial activity of complex **1** against *S. epidermidis*, *B. cereus* and *E. coli* is better than complex **2**, its activity against *L. monocytogenes* is lower than complex **2**.

While the complex **2** and free ligand are inactive, against *K. pneumoniae* just complex **1** has strong activity (inhibitory zones ≥ 35).[11] It should be noticed that the antibacterial activity of two complexes are higher than standard antibiotic (gentamicin) against *S. epidermidis* and *B. cereus*. Also, antibacterial activity of complex **1** is higher than standard antibiotic against *L. monocytogenes*, *K. pneumoniae*and and *E. coli*. Against all tested bacteria, free Clphtpy ligand is inactive. The higher activity of complexes may be explained on the basis of chelation theory.[11] The antibacterial effects of $Cd(OAc)_2$, $Cd(NO_3)_2$ and NaN_3 as a control are shown in Table 4. According to the antibacterial activities of NO_3^- and N_3^- anions, we can say that part of antibacterial activity of complexes are due to the presence of these anions in considered structures of theirs.[12–13] Against *P. aeruginosa*, all of the considered compounds including complexes **1**–**2**, anions and free ligand are inactive. While two synthesized complexes and free ligand against *S. agalactiae* and *E. aerogenes* were inactive, acetate and nitrate salts of cadmium, also azide anion against these bacteria had mild or good activity. These results show that cadmium nitrate has higher antibacterial effects against *S. agalactiae* and *E. aerogenes* – when it is used individually compared to ligand itself and complexes **1**–**2**. However the mixture of cadmium nitrate and ligand as a complex show high or equal antibacterial activity against *B. cereus* and *E. coli* compared to cadmium nitrate and free ligand. So it can be

Table 4. Antibacterial activity of Clphtpy ligand, salts, Cd(II) complexes and gentamicin (as a standard compound).

Growth Inhibitory zone (mm)							
Microorganism	Complex 1	Complex 2	L	$Cd(NO_3)_2$	$Cd(OAc)_2$	NaN_3	Gentamicin
S. epidermidis	40	20	–	35	40	–	15
S. agalactiae	–	–	–	30	30	30	10
L. monocytogenes	20	25	–	20	25	45	20
B. cereus	40	35	–	30	30	25	15
E. aerogenes	–	–	–	30	25	20	10
K. pneumoniae	35	–	–	25	10	20	10
P. aeruginosa	–	–	–	–	–	–	10
E. coli	30	10	–	10	10	–	20
Minimum inhibitory concentration (mg/ml)							
S. epidermidis	1.56	25	–	3.125	1.56	–	
S. agalactiae	–	–	–	6.25	6.25	6.25	
L. monocytogenes	25	12.5	–	25	12.5	1.78	
B. cereus	1.56	3.125	–	6.25	6.25	12.5	
E. aerogenes	–	–	–	6.25	12.5	25	
K. pneumoniae	3.125	–	–	12.5	100	25	
P. aeruginosa	–	–	–	–		–	
E. coli	6.25	100	–	100	100	–	

concluded that even though cadmium nitrate has higher antibacterial effects and this combination reduce its activity, the complexes still show significant activity that may in part be associated with the presence of Cd, ligand and specially anions.[24–25] The molecular mechanism of the antibacterial activity of these complexes may be related to their effects on the bacterial plasma or cytoplasmic membrane which is associated with many important enzymes and as an important target site for these complexes with anions. In addition to their effects on bacterial enzymes, it is possible that these complexes inhibit bacterial growth and cell division and damage the cell envelope and contents of bacteria.[24–25] MIC is the lowest concentration of an antimicrobial agent that will inhibit the visible growth of a microorganism after incubation and its amount shows resistance of microorganisms to an antimicrobial agent. In this article MIC amounts are 1.56–100 mg/ml, which are not so high. 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. We have used different terpyridine based cadmium complexes on different bacteria.[7–9] The results clearly showed that the Cd(II) complexes with NO_3^- possess significant antibacterial activity against the tested strains, as cadmium alters mainly the bacterial metabolism in pathways implying sugars, purine, phosphate, calcium signaling and cell respiration, cadmium toxicity could be increased by NO_3^-, or the same as silver nitrate which causes formation of shrunken cells and DNA fragmentation in B. licheniformis, Cd(II) complexes with nitrate might have the same effects on the tested bacteria.

5. Electronic Absorption and Emission Properties

Electronic spectra of the compounds were recorded in DMSO medium. In comparison with free Clphtpy ligand, for both complexes the intense absorption peaks and shoulders at ca. 280–320 nm are assigned to intraligand (IL) transitions (Fig. 5a).[26] Due to the presence of 4-Clphenyl substituent on the tpy-H ligand, the extinction coefficients of the absorption bands are high. As it is clear, similar absorption spectra are obtained for both complexes with similar chromophore units. Accordingly, emission spectra of ligand and complexes are very similar and a small blue shift occurred in the maximal absorption peak. Relative to ligand, the fluorescence intensity of complexes are stronger (by a factor of ca. 3.5 for complex **1** and **2**) (Fig. 5b). On the other hand, the shape and position of the fluorescence emission bands are not different. It seems that emission intensities change is a function of complex structures.

6. Thermal Properties

The thermal behaviors of complexes were ascertained by thermo gravimetric analysis (TGA) and difierential thermal analyses (DTA) in air between 50–800 °C with the heating rate of 10 °Cmin^{-1}. TG analysis of **1** and **2** shows remarkable stability of the frameworks for both complexes to 400 °C and 325 °C, respectively. The thermal decomposition of the compounds follows a four-step mechanism with endothermic effects. For **1**, the first step occurs at a maximum lying in the region of 400–430 °C. The weight loss in this step agrees with the loss of two coordinated water and nitrate molecules (observed: 25.54%, calcd: 23.71%). Next steps in the degradation of the complex **1** occur in the region around 450–650 °C and might be associated with the loss of the Clphtpy ligand (observed: 51.92%, calcd: 54.76%). The final decomposition product was CdO as confirmed by qualitative analysis (observed: 22%, calcd: 21%) (Fig. 6a). Due to the loss of three coordination azide molecules for complex **2**, TGA result indicates the first weight loss of 13.34% occur from 325 to 350 °C, which is consistent

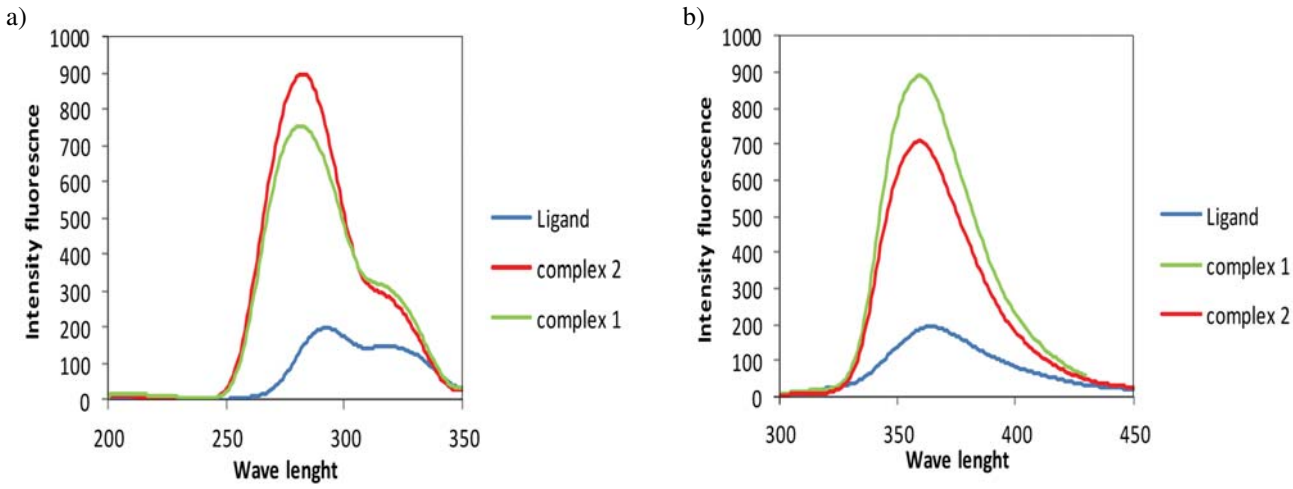
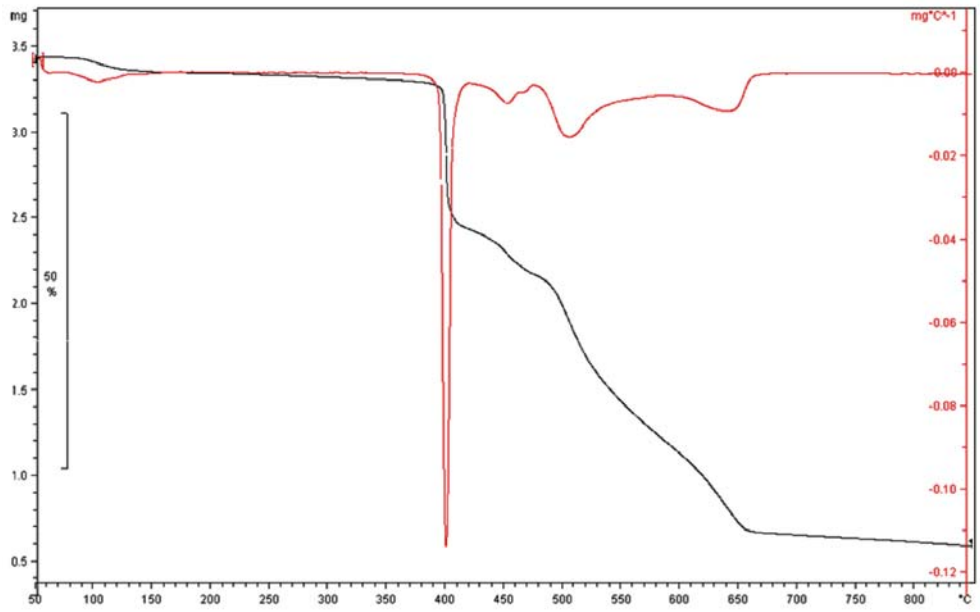


Fig. 5. UV absorption (a) and emission (b) spectra of the free Clphtpy ligand and complexes **1** and **2**

with the calculated value 11.64%. Further heating to 700 °C led to separation of organic compounds (observed: 60.66%, calcd: 63.62%) and the final inorganic residue (CdO) was obtained (observed: 26%, calcd: 24%) which is in good agreement of two Cd atoms in dimeric structure of **2** (Fig. 6b). Both complexes showed good thermal

a)



b)

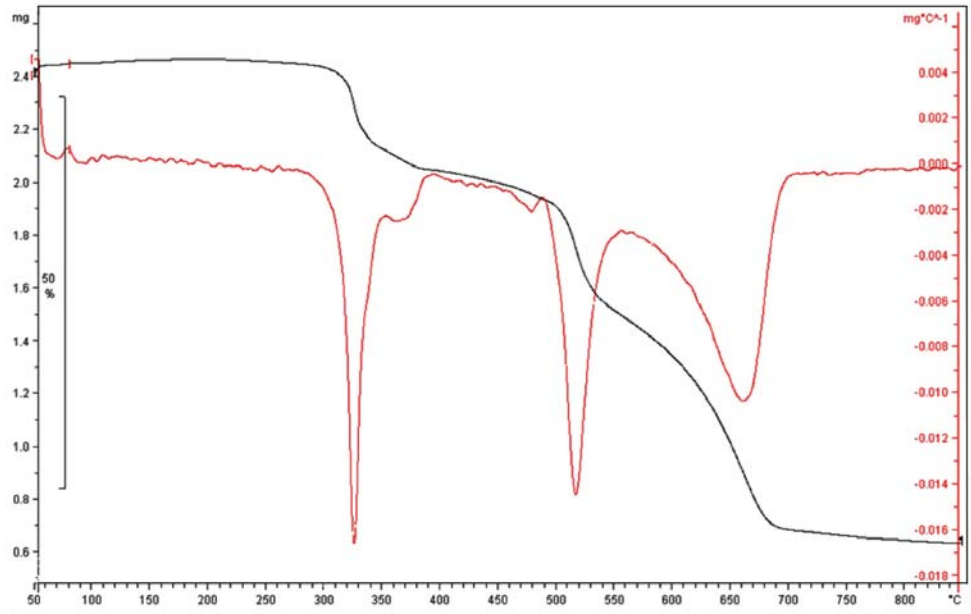


Fig. 6. Thermogravimetric (TG, black scale) and differential thermal analysis (DTA, red scale) of complex **1** (a) and complex **2** (b)

stability indicating their suitability for electronic device applications.[27]

7. Conclusions

In this paper we reported the synthesis, characterization and photophysical studies of two new cadmium-Clphtpy complexes with metal to ligand ratio of 1:1. We found that by changing counter ions (from NO_3^- to N_3^-) the compounds had been developed from mononuclear complexes to independent dinuclear dimers. These results proved that it was an effective way to synthesize different cadmium complexes of Clphtpy. The antibacterial properties of the synthesized complexes, ligand and salts were examined. The bioassay results demonstrated the free li-

gand is inactive against all tested bacteria but complexes have good activity. The higher activity of complexes may be explained on the basis of chelation theory. Both complexes showed good thermal stability indicating their suitability for electronic device applications.

8. Acknowledgement

This work was supported by the Payame Noor University in I. R. of Iran and the University of di Messina in Italy has provided the funds for running the X-ray Service Center at the Chemistry Department.

9. Appendix A. Supplementary Data

CCDC reference numbers 894581 & 894582 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

9. References

1. X. Chen, Q. Zhou, Y. Cheng, Y. Geng, D. Ma, Zh. Xie, L. Wang, *J. Lumin.* **2007**, *126*, 81–90.
2. W. Huang, H. Qian, *J. Mol. Struct.* **2007**, *832*, 108–116.
3. W. Huang, W.You, L. Wang, Ch. Yao, *Inorg. Chim. Acta* **2009**, *362*, 2127–2135.
4. W. Huang, H. Qian, *J. Mol. Struct.* **2008**, *874*, 64–76.
5. H. Feng, X. -Ping Zhou, T. Wu, D. Li, Y. -G. Yin, S. Weng Ng, *Inorg. Chim. Acta* **2006**, *359*, 4027–4035.
6. A. Nemati Kharat, A. Bakhoda, S. Zamanian, *Polyhedron* **2011**, *30*, 1134–1142.
7. L. A. Saghatforoush, L. Valencia, F. Chalabian, S. Ghammamy, *Bioinorganic Chemistry and Applications,* DOI: 10.1155/2011/803292
8. L. A. Saghatforoush, L. Valencia, F. Chalabian, S. Ghammamy, L. Z. Khaledi, *J. Coord. Chem.* **2011**, *64*, 3311–3322.
9. a) L. A. Saghatforoush, L. Valencia, F. Chalabian, S. Ghammamy, F. Katouzian, *J. Chem. Sci.* **2012**, *124*, 577-585, b) L. A. Saghatforoush, S. G. Telfer, F. Chalabian, R. Mehdizadeh, R. Golbedaghi, G. H. Shahverdizadeh, *J. Coord. Chem.* **2011**, *64*, 2186–2201.
10. A. Baver, W. M. M. Kirby, J. E. Sherris, M. Turck, *J. Clin. Pathol*. **1989**, *45*, 493–496.
11. a) L. A. Saghatforoush, F. Chalabian, A. Aminkhani, G. Karimnezhad, S. Ershad, *Eur. J. Med. Chem*. **2009**, *44*, 4490–4495, b) K.-B. Chew, M. T. H. Tarafder, K. A. Crouse, A. M. Al, B. M. Yamin, H. -K. Fun, *Polyhedron* **2004**, *23*, 1385–1392.
12. S. D. Cummings, *Coord. Chem. Rev*. **2009**, *253*, 1495–1516.
13. A. Jain, B. S. J. Winkel, K. J. Brewer, *J. Inorg. Bio Chem*. **2007**, *101*, 1525–1528.
14. a) COSMO, version 1.60; Bruker AXS Inc.: Madison, Wisconsin, **2005**. b) SAINT, version 7.06A; Bruker AXS Inc.: Madison, Wisconsin, **2005**. c) SADABS, version 2.10; Bruker AXS Inc.: Madison, Wisconsin, **2005**.
15. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, SIR2004, *J. Appl. Crystallogr.***2005**, *38*, 381–388.
16. Sheldrick, G. M. SHELXL97, University of Göttingen, Göttingen, Germany, **1997**.
17. Y.-B. Dong, R. C. Layland, M. D. Smith, N. G. Pschirer, U. H. F. Bunz, H.-C. zurLoye, *Inorg. Chem*. **1999**, *38*, 3056–3060.
18. M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 7287–7288.
19. M. B. Zaman, M. D. Smith, H.-C.zurLoye, *Chem. Mater*. **2001**, *13*, 3534–3541.
20. a) H. Seto, A. Tomasz, *Proc.Nat. Acad. Sci. U.S.A*. **1977**, *74*, 296–299; b) G. Lowe, A.S. Droz., T. Vilaivan, G. W. Weaver, L. Twee dale, J. M. Pratt, P. Rock, V. Yardley, S. L. Croft, *J. Med. Chem*. **1999**, *42*, 999–1006.
21. J. Granifo, M. T. Garland, R. Baggio, *Inorg. Chem. Commun*. **2004**, *7*, 77–81.
22. Z. Ma, B. Liu, H. Yang, Y. Xing, M. Hu, J. Sun, *J. Coord. Chem.* **2009**, *62*, 3314–3323.
23. J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Ltd., Chicheste, UK, **2000**.
24. V. M. E. Marshall and B. Reiter, *J. Gen. Microbiol* **1980**, *120*, 513–516.
25. Z. H. Chohan and M. Praveen, *Metal-Based Drugs*. **1999**, *6*, 95–99.
26. K. K.-W. Lo, C.-K. Chung, D. C.-M. Ng, N. Zhu, *New J. Chem*. **2002**, 26, 81–88.
27. S.-H. Hwang, C. N. Moorefield, P. Wang, J.-Y.Kim, S.-W. Lee, G. R. Newkome, *Inorg. Chim.Acta* **2007**, *360*, 1780–1784.

Povzetek

Sintetizirali smo dve novi koordinacijski spojini Cd(II) s 4'-(4-klorofenil)-2,2':6',2''-terpiridinom (Clphtpy) kot ligandom. Kompleksa s sestavo $[Cd(Clphtpy)(NO_3)_2H_2O]$ (**1**) in $[Cd(Clphtpy)(N_3)_2]_2$ (**2**) smo okarakterizirali s CHN elementno analizo, FT-IR, ^1H NMR, absorpcijsko in emisijsko spektroskopijo, termično analizo in rentgensko strukturno analizo na monokristalu. Rezultati rentgenske strukturne analize so pokazali, da sta koordinacijski števili v spojinah **1** in **2** sedem in šest, s koordinacijskima poliedroma N_3O_4 oziroma N_6. Antibakterijsko aktivnost smo testirali proti štirim gram-pozitivnim in štirim gram-negativnim bakterijam. Rezultati biološke študije so pokazali, da ima koordinacijska spojina **1** zelo dobro aktivnost proti večini testiranih bakterij in da je njena aktivnost boljša od standardnega antibiotika gentamicina.