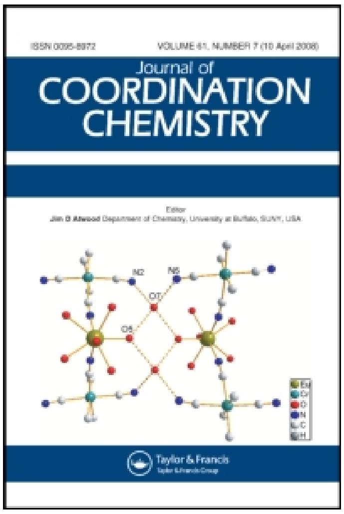

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Studies on two cadmium(II) and two zinc(II) complexes of 4′-chloro-2,2′ : 6′,2″-terpyridine with 1 : 1 or 1 : 2 ratio of metal and ligand

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The reaction between 4′-chloro-2,2′ : 6′,2″-terpyridine (tpyCl) with d^{10} transition-metal ions produced two cadmium(II) and two zinc(II) metal complexes, formulated as [Cd(tpyCl-κ^3N,N',N'')(NO_3-κ^2O,O')(NO_3-κO)(H_2O-κO)] (**1**), [Cd(tpyCl-κ^3N,N',N'')$_2$](ClO_4)$_2$ (**2**), [Zn(tpyCl-κ^3N,N',N'')$_2$](ClO_4)$_2$ (**3**), and [Zn(tpyCl-κ^3N,N',N'')$_2$](BF_4)$_2$ (**4**). Supramolecular interactions include coordinative bonding, O–H···O, O–H···Cl, C–H···F, and C–H···Cl hydrogen bonding and π–π stacking, all of which play essential roles in forming different frameworks of **1**–**4**.

Keywords: 4′-chloro-2,2′ : 6′,2′-terpyridine; d^{10} Transition-metal ion complexes; Supramolecular interactions; Crystal structures

1. Introduction

Since 2,2′ : 6′,2″-terpyridine (tpy) was first prepared [1, 2], this tridentate ligand, along with its substituted analogues, has been widely studied due to applications in drug design, material chemistry, and photofunctional supramolecular assemblies [3–8]. The ability of tpy to chelate a wide range of metal ions has led to its incorporation in macrocyclic ligands [9–12]. Lanthanide complexes of tpy ligands with multiple pendant carboxylate groups are attracting interest as luminescent agents for protein labeling [13–16]. The design of multi-nucleating ligands incorporating two or more remote tpy metal-binding domains permit extension of this area of coordination chemistry from the molecular to the supramolecular level [17–20].

Synthesis of substituted analogues has been extensively studied by Constable's group [21]. For example, they prepared a series of fullerene-functionalized tpy ligands and investigated their coordination behavior, where significant interactions between C60

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and a directly linked tpy residue have been detected [21a]. Additionally, Sjödin *et al.* [22] investigated the Mn(III)/Mn(II) reduction potential for a series of 4′-substituted terpyridine ligands together with the corresponding values for the iron substituted 4′-substituted terpyridine complexes which changed linearly with their Hammett constants σ_{Para}.

Our purpose is to use this rigid tridentate ligand to form 1 : 1 4′-chloro-2,2′ : 6′, 2″-terpyridine (tpyCl) metal complexes where some coordination sites of metal are not occupied, to utilize as building blocks to assemble multi-functional coordination polymers or supramolecular networks exhibiting fluorescence and optoelectric properties [23, 24]. In our previous work, we have reported the structural comparison of hydrochlorate tetrafluoroborate and hydrochlorate hexafluorophosphorate of tpyCl with C–H ⋯ X hydrogen bonding interactions [25], and Ru(II), Cu(II), Zn(II), Ni(II), and Fe(II) complexes of tpyCl including a five-coordinate zinc(II) complex $[\mathrm{Zn}(\mathrm{L}\text{-}\kappa^3 N,N',N'')\mathrm{Cl}_2]$ with 1 : 1 metal : ligand ratio [26]. In this article, we extend our studies on the coordination chemistry of d^{10} transition-metal ions with different counterions and report the preparation and structural characterization of two cadmium(II) and two zinc(II) complexes, $[\mathrm{Cd}(\mathrm{tpyCl}\text{-}\kappa^3 N,N',N'')(\mathrm{NO_3}\text{-}\kappa^2 O,O')(\mathrm{NO_3}\text{-}\kappa O)(\mathrm{H_2O}\text{-}\kappa O)]$ (**1**), $[\mathrm{Cd}(\mathrm{tpyCl}\text{-}\kappa^3 N,N',N'')_2](\mathrm{ClO_4})_2$ (**2**), $[\mathrm{Zn}(\mathrm{tpyCl}\text{-}\kappa^3 N,N',N'')_2](\mathrm{ClO_4})_2$ (**3**), and $[\mathrm{Zn}(\mathrm{tpyCl}\text{-}\kappa^3 N,N',N'')_2](\mathrm{BF_4})_2$ (**4**).

2. Experimental

2.1. *Materials and measurements*

4′-Chloro-2,2′ : 6′,2″-terpyridine is commercially available from Aldrich and was used as received. All other solvents and reagents were of analytical grade and used without purification. Elemental analyses (EA) for carbon, hydrogen, and nitrogen were performed on a Perkin–Elmer 1400C analyzer. Infrared (IR) spectra (4000–400 $\mathrm{cm^{-1}}$) were recorded with a Nicolet FT-IR 170X spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of 100–1200 amu. UV–Vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a Pyrex cell with a path length of 10 mm at room temperature. ^{1}H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS ($\mathrm{SiMe_4}$) as an internal reference at room temperature.

2.2. *Syntheses and characterizations*

Caution: Although no problem was encountered in our experiments, transition metal perchlorates are potentially explosive and should be handled in small quantities.

2.2.1. Synthesis of (1). A colorless methanol solution (10 $\mathrm{cm^3}$) of $\mathrm{Cd(NO_3)_2 \cdot 4H_2O}$ (0.077 g, 0.25 mmol) was added to 4′-chloro-2,2′ : 6′,2″-terpyridine (0.0669 g, 0.25 mmol) dissolved in 20 $\mathrm{cm^3}$ methanol at room temperature. The mixture was stirred at room temperature for 1 h and then slowly evaporated in air to near 5 $\mathrm{cm^3}$. The resulting microcrystals were collected, washed by acetone and dried *in vacuo*. Yield: 0.100 g, 76%. Anal. Calcd for $CdC_{15}H_{12}N_5O_7Cl$: C: 34.50, H: 2.32, N: 13.41%. Found: C: 34.42, H: 2.29, N: 13.42%. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3375 (b), 3068 (s), 1637 (w), 1587 (s), 1559 (s), 1476 (s), 1388 (vs), 1247 (m), 1300 (s), 1162 (m), 1128 (m), 1119 (m), 1051 (m), 1040 (m), 1013 (s), 884 (m), 828 (s), and 795 (s). ^1H NMR (CD_3OD): 8.86–8.82 (m, 4H), 8.72 (d, 2H), 8.32 (dd, 2H), and 7.85 (dd, 2H). ESI-MS in methanol: *m*/*z* 460 $[Cd(C_{15}H_{10}N_3Cl)(NO_3)(H_2O)]^+$. UV–Vis in MeOH: 328, 317, 283, 277, 269, and 236 nm. Single crystals of (**1**) suitable for X-ray diffraction measurement were obtained from methanol and water solution at a ratio of 3 : 1 by slow evaporation in air at room temperature.

2.2.2. Syntheses of (2)–(4). Complexes **2** and **3** were prepared by treatment of 1 : 2 molar ratio of corresponding metal salts ($Cd(ClO_4)_2 \cdot 6H_2O$ or $Zn(ClO_4)_2 \cdot 6H_2O$) and tpyCl in 20 cm^3 ethanol. The mixture was stirred for 2 h at ambient temperature and then slowly evaporated in air. In the case of **4**, excess $NaBF_4$ was added to the solution and the resulting precipitates were collected, washed by a small amount of cold ethanol and dried *in vacuo*. Yields of **2**–**4**: 70–80%. Characterizations of **2**–**4**: Anal. Calcd for $CdC_{30}H_{20}Cl_4N_6O_8$ (**2**): C: 42.55, H: 2.38, N: 9.93%. Found: C: 42.60, H: 2.31, N: 9.96%. Anal. Calcd for $ZnC_{30}H_{20}Cl_4N_6O_8$ (**3**): C: 45.06, H: 2.52, N: 10.51%. Found: C: 45.10, H: 2.48, N: 10.59%. Anal. Calcd for $ZnC_{30}H_{20}Cl_2N_6B_2F_8$ (**4**): C: 46.53, H: 2.60, N: 10.85%. Found: C: 46.56, H: 2.64, N: 10.79%. ESI-MS of **2** in methanol: *m*/*z* 480 $[Cd(C_{15}H_{10}N_3Cl)(ClO_4)]^+$; ESI-MS of **3** in methanol: *m*/*z* 432 $[Zn(C_{15}H_{10}N_3Cl)(ClO_4)]^+$; ESI-MS of **4** in methanol: *m*/*z* 420 $[Zn(C_{15}H_{10}N_3Cl)(BF_4)]^+$. Compounds **2** and **3** have identical FT-IR absorptions at 3439 (b), 3069 (w), 1595 (m), 1560 (w), 1476 (s), 1421 (w), 1304 (w), 1249 (m), 1195 (s), 1144 (s), 1104 (m), 1088 (m), 957 (s), 830 (w), 638 (s), and 621 (m). Main FT-IR absorptions (KBr pellets, cm^{-1}) for **4**: 3437 (m), 1598 (s), 1568 (m), 1558 (m), 1475 (s), 1423 (s), 1339 (m), 1248 (m), 1083 (m), 1059 (vs), 834 (s), 793 (w), 728 (s), and 576 (s). Compounds **2**–**4** have analogous UV–Vis absorptions in MeOH (Supplementary Material). **2**: 328, 317, 283, and 237 nm; **3**: 330, 319, 284, 276, 268, and 237 nm; **4**: 329, 318, 283, 275, 267, and 236 nm. Similarly, **2**–**4** have almost the same ^1H NMR spectral data in DMSO-d^6: 8.75–8.62 (m, 8H), 8.43 (s, 4H), 8.06–8.03 (dd, 4H), and 7.57–7.54 (dd, 4H). All the above-mentioned FT-IR, UV–Vis, and ^1H NMR spectra of **2**–**4** are comparable with our previously reported 1 : 2 metal-ligand complexes [26]. Single crystals of **2**–**4** suitable for X-ray diffraction were obtained from a mixture of methanol and ethanol by slow evaporation in air at ambient temperature.

2.3. *X-ray data collection and solution*

Single-crystal samples of **1**–**4** were glue-covered, mounted on glass fibers and then used for data collection. Crystallographic data of **1** were collected at 291(2) K on a Rigaku Mercury CCD area-detector, while those of **2**–**4** were collected at 291(2) K on a Bruker SMART 1K CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). In the case of the Rigaku system, the original data file (*.dat) generated by Crystalclear [27] was transformed to SHELXTL97 format (*.*hkl*) by TEXSAN program [28]. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares on F^2_{obs} by using the SHELXTL-PC software package [29]. All nonhydrogen atoms were anisotropically refined and all hydrogens were inserted in the calculated positions, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent atoms. One oxygen (O4) from one of the two perchlorate anions in **2** is refined disordered over two sites with 0.54 : 0.46 site occupancy factors. In the case of **3**, "TWIN" instruction was used to refine the structure, otherwise it gave a high Flack parameter of 0.38(3). The summary of the crystal data, experimental details, and refinement results for **1–4** is listed in table 1, while selected bond distances and angles are given in table 2 for **1** and in table 3 for **2–4**. Table 4 contains hydrogen-bond parameters for **1–4**.

3. Results and discussion

3.1. *Single-crystal structure of [Cd(tpyCl-κ^3N,N′,N″)(NO$_3$-κ^2O,O′)(NO$_3$-κO)(H$_2$O-κO)] (1)*

The atom-numbering scheme of **1** is shown in figure 1, with Cd(II) seven-coordinate by three nitrogens and four oxygens in a pentagonal bipyramid coordination geometry. Three nitrogens (N1, N2, and N3) from the tridentate tpyCl and two oxygens (O1 and O2) of one nitrate constitute the basal plane with mean deviation from least-squares plane as 0.0860 Å, while one oxygen from the other nitrate and one oxygen from the coordinating water occupy the two apical positions. Every pyridine ring is essentially planar; dihedral angles between the middle ring and two side rings are 8.2° and 8.7° and both bend to the same direction of the molecular plane. Intramolecular hydrogen bonds between the pyridyl hydrogens and the nitrate oxygens (C1–H1 ⋯ O1 and C15–H15 ⋯ O2) are responsible for the torsion. The structural parameters in **1** are in agreement with those found in previously reported similar compounds [25, 26] and another Cd(II) complex [Cd(4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine)(NO_3)$_2$(H_2O)] reported by Granifo *et al.* [30].

In the packing of **1**, a 12-membered parallelogram carbon-free hydrogen-bond ring ($Cd_2N_2O_6H_2$) is formed where two Cd(II) ions and two coordinating waters from two adjacent molecules occupy alternately the apexes (figure 2). The Cd(II) ⋯ Cd(II) distance of this dimeric structure is 6.699 Å. Neighboring dimeric structures are linked by two additional O–H ⋯ O hydrogen bonds between coordinated water (O7) and one of the oxygens of nitrate (O5), with Cd(II) ⋯ Cd(II) separations of 7.188 and 7.768 Å. A 1-D hydrogen-bond-sustained structure is constructed where Cd(II) ions are arranged in a zigzag way. The 1-D chain is further packed into a 3-D layer structure where weak C–H ⋯ O hydrogen bonds between the pyridyl carbon atoms (C7 and C12) and the oxygen atoms of nitrate (O5 and O3) link to the adjacent chains. In addition, all the tpyCl rings in the crystal packing of **1** are parallel and π–π stacking interactions are found between each side ring of tpyCl and another contiguous counterpart with the centroid–centroid separation of 3.787 Å. Thus, a 3-D framework sustained by hydrogen-bonding and π–π stacking interactions is formed.

Table 1. Crystal data and structural refinements for **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$CdC_{15}H_{12}ClN_5O_7$	$CdC_{30}H_{20}Cl_4N_6O_8$	$ZnC_{30}H_{20}Cl_4N_6O_8$	$ZnC_{30}H_{20}Cl_2N_6B_2F_8$
Formula weight	522.15	846.72	799.69	774.41
T (K)	291(2)	291(2)	291(2)	291(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	Cc	$P2_1/n$
Units of dimensions (Å, °)				
a	7.768(2)	9.067(1)	12.807(2)	8.785(3)
b	10.025(2)	8.956 (1)	12.333(2)	8.872(3)
c	12.505(3)	40.231(5)	20.355(4)	39.957(13)
α	74.73(3)	90	90	90
β	78.09(3)	92.68(1)	98.44(1)	95.39 (1)
γ	74.60(3)	90	90	90
V (Å^3)	895.9(4)	3263.6(7)	3180.2(10)	3100.5(18)
Crystal size (mm^3)	0.10 × 0.10 × 0.20	0.10 × 0.12 × 0.16	0.10 × 0.12 × 0.16	0.10 × 0.10 × 0.12
Z	2	4	4	4
D_{Calcd} (mg m^{-3})	1.936	1.723	1.670	1.659
μ (Mo-Kα) (mm^{-1})	1.421	1.057	1.171	1.047
$F(000)$	516	1688	1616	1552
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Data collected/unique	7562/3072	15,853/5732	7929/3773	30,786/5468
Limiting indices	$-9 \le h \le 8$ $-11 \le k \le 11$ $-13 \le l \le 14$	$-10 \le h \le 7$ $-9 \le k \le 10$ $-47 \le l \le 47$	$-15 \le h \le 10$ $-14 \le k \le 14$ $-19 \le l \le 24$	$-10 \le h \le 8$ $-10 \le k \le 10$ $-47 \le l \le 47$
Max./min. transmission	0.8710/0.7643	0.9016/0.8490	0.8919/0.8348	0.9025/0.8846
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0345$, $wR_2 = 0.0776$	$R_1 = 0.0532$, $wR_2 = 0.0825$	$R_1 = 0.0548$, $wR_2 = 0.0822$	$R_1 = 0.0715$, $wR_2 = 0.0967$
R_1, wR_2 (all data)	$R_1 = 0.0392$, $wR_2 = 0.0793$	$R_1 = 0.1118$, $wR_2 = 0.1094$	$R_1 = 0.1628$, $wR_2 = 0.1073$	$R_1 = 0.1655$, $wR_2 = 0.1138$
Goodness-of-fit on F^2	1.149	0.825	0.648	0.916
Δ (e Å^{-3}) (max, min)	0.53/−0.63	0.56/−0.58	0.40/−0.33	0.77/−0.62

Note: $R_1 = \sum ||F_o| - |F_c|| \sum F_o|$, $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg) for $[ML]^{2+}$ complex (**1**).

Bond distances		Bond angles	
1			
Cd1–O1	2.446(3)	O1–Cd1–O2	51.71(9)
Cd1–O2	2.456(3)	O1–Cd1–O4	74.88(11)
Cd1–O4	2.331(3)	O1–Cd1–O7	93.91(11)
Cd1–O7	2.340(3)	O1–Cd1–N1	84.42(10)
Cd1–N1	2.386(3)	O1–Cd1–N2	153.29(9)
Cd1–N2	2.331(3)	O1–Cd1–N3	136.05(9)
Cd1–N3	2.354(3)	O2–Cd1–O4	83.92(12)
		O2–Cd1–O7	84.62(11)
		O2–Cd1–N1	134.97(11)
		O2–Cd1–N2	155.00(10)
		O2–Cd1–N3	85.22(10)
		O4–Cd1–O7	167.42(11)
		O4–Cd1–N1	94.98(12)
		O4–Cd1–N2	101.31(12)
		O4–Cd1–N3	94.50(12)
		O7–Cd1–N1	89.47(10)
		O7–Cd1–N2	91.27(11)
		O7–Cd1–N3	89.70(11)
		N1–Cd1–N2	69.43(10)
		N1–Cd1–N3	139.46(10)
		N2–Cd1–N3	70.07(10)

Table 3. Selected bond distances (Å) and angles (deg) for ML_2 complexes (**2**–**4**).

Bond distances		Bond angles	
2			
Cd1–N1	2.337(5)	N1–Cd1–N2	70.09(18)
Cd1–N2	2.281(4)	N1–Cd1–N3	140.10(18)
Cd1–N3	2.327(5)	N1–Cd1–N4	93.26(17)
Cd1–N4	2.387(5)	N1–Cd1–N5	108.72(18)
Cd1–N5	2.279(5)	N1–Cd1–N6	95.66(18)
Cd1–N6	2.287(6)	N2–Cd1–N3	70.40(18)
		N2–Cd1–N4	95.91(18)
		N2–Cd1–N5	165.56(18)
		N2–Cd1–N6	123.20(18)
		N3–Cd1–N4	96.05(18)
		N3–Cd1–N5	110.91(19)
		N3–Cd1–N6	101.18(18)
		N4–Cd1–N5	69.68(19)
		N4–Cd1–N6	140.6(2)
		N5–Cd1–N6	71.1(2)
3			
Zn1–N1	2.168(10)	N1–Zn1–N2	76.0(5)
Zn1–N2	2.061(12)	N1–Zn1–N3	151.5(4)
Zn1–N3	2.186(12)	N1–Zn1–N4	94.0(4)
Zn1–N4	2.138(11)	N1–Zn1–N5	107.2(5)
Zn1–N5	2.055(12)	N1–Zn1–N6	93.6(4)
Zn1–N6	2.154(10)	N2–Zn1–N3	75.5(5)
		N2–Zn1–N4	101.9(5)
		N2–Zn1–N5	175.2(5)
		N2–Zn1–N6	106.8(5)
		N3–Zn1–N4	93.4(4)
		N3–Zn1–N5	101.4(5)

(*Continued*)

Table 3. Continued.

Bond distances		Bond angles	
		N3–Zn1–N6	93.1(4)
		N4–Zn1–N5	74.6(5)
		N4–Zn1–N5	151.4(5)
		N5–Zn1–N6	76.8(5)
4			
Zn1–N1	2.177(5)	N1–Zn1–N2	75.5(2)
Zn1–N2	2.079(5)	N1–Zn1–N3	151.8(2)
Zn1–N3	2.169(5)	N1–Zn1–N4	94.17(19)
Zn1–N4	2.200(5)	N1–Zn1–N5	104.2(2)
Zn1–N5	2.069(5)	N1–Zn1–N6	93.8(2)
Zn1–N6	2.151(5)	N2–Zn1–N3	76.4(2)
		N2–Zn1–N4	101.5(2)
		N2–Zn1–N5	176.8(2)
		N2–Zn1–N6	107.6(2)
		N3–Zn1–N4	93.7(2)
		N3–Zn1–N5	104.1(2)
		N3–Zn1–N6	92.33(19)
		N4–Zn1–N5	75.3(2)
		N4–Zn1–N6	150.9(2)
		N5–Zn1–N6	75.6(2)

Table 4. Hydrogen bonding interactions (Å, °) in **1**–**4**.

D–H · · · A	D–H	H · · · A	D · · · A	∠DHA	Symmetry code
1					
O7–H7A · · · O5	0.85	2.04	2.869(5)	163.0	$1+x, y, z$
O7–H7B · · · O3	0.85	2.04	2.857(4)	160.0	$1-x, -y, 1-z$
C1–H1 · · · Cl1	0.93	2.78	3.475(4)	132.0	$1+x, -1+y, z$
C1–H1 · · · O1	0.93	2.52	3.168(4)	127.0	
C7–H7 · · · O5	0.93	2.45	3.322(5)	156.0	$-x, 1-y, -z$
C12–H12 · · · O3	0.93	2.35	3.222(5)	155.0	$-1+x, 1+y, z$
C15–H15 · · · O2	0.93	2.52	3.190(5)	129.0	
2					
C4–H4 · · · O5	0.93	2.55	3.332(8)	142.0	$1-x, 1-y, -z$
C16–H16 · · · O7	0.93	2.58	3.243(12)	129.0	$-1+x, y, z$
C18–H18 · · · O1	0.93	2.53	3.315(14)	142.0	$-1+x, -1+y, z$
C22–H22 · · · O2	0.93	2.51	3.350(13)	151.0	$1/2-x, -1/2+y, 1/2-z$
C24–H24 · · · O1	0.93	2.55	3.471(12)	172.0	$3/2-x, -1/2+y, 1/2-z$
C28–H28 · · · Cl2	0.93	2.71	3.562(11)	153.0	$3/2-x, 1/2+y, 1/2-z$
3					
C7–H7 · · · O3	0.93	2.52	3.37(3)	153.0	$1/2+x, 3/2-y, 1/2+z$
C13–H13 · · · O5	0.93	2.46	3.37(3)	169.0	$-1/2+x, 1/2+y, z$
C14–H14 · · · O1	0.93	2.57	3.19(2)	124.0	$x, y, 1+z$
C19–H19 · · · O7	0.93	2.50	3.36(3)	154.0	$1/2+x, 1/2-y, 1/2+z$
C28–H28 · · · Cl3	0.93	2.74	3.358(19)	125.0	$x, 2-y, 1/2+z$
4					
C1–H1 · · · F1	0.93	2.55	3.340(9)	143.0	
C3–H3 · · · F8	0.93	2.51	3.364(9)	152.0	
C7–H7 · · · F5	0.93	2.51	3.440(8)	174.0	
C12–H12 · · · F7	0.93	2.38	3.172(8)	143.0	
C16–H16 · · · F6	0.93	2.53	3.311(8)	141.0	
C18–H18 · · · F2	0.93	2.51	3.401(10)	159.0	$x, 1+y, z$
C22–H22 · · · F4	0.93	2.55	3.436(10)	160.0	$x, 1+y$, z
C27–H27 · · · F3	0.93	2.40	3.259(10)	154.0	$-x, 1-y, 1-z$
C28–H28 · · · Cl2	0.93	2.72	3.388(7)	129.0	$-x, -1/2+y, 3/2-z$
C30–H30 · · · F5	0.93	2.50	3.387(8)	159.0	$1-x, 1-y, 1-z$

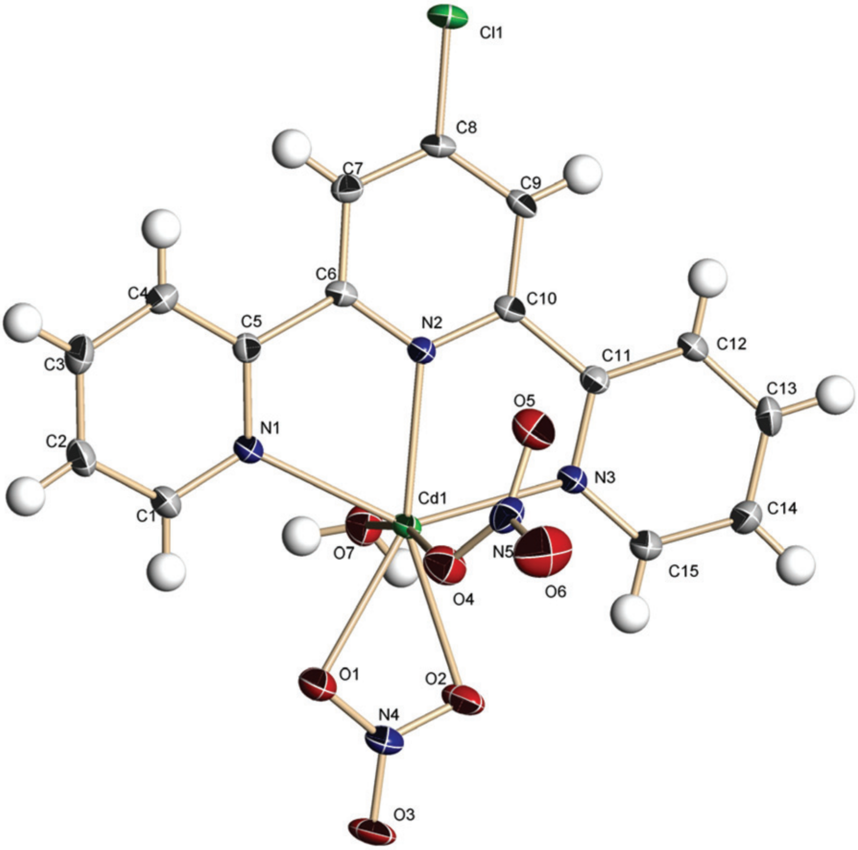

Figure 1. An ORTEP drawing of **1** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii.

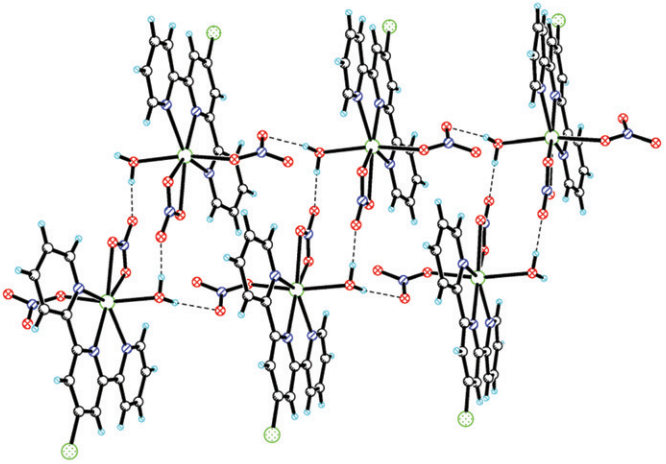

Figure 2. A perspective view of the intermolecular hydrogen-bond contacts in **1**. Hydrogen bonds are indicated as dashed lines.

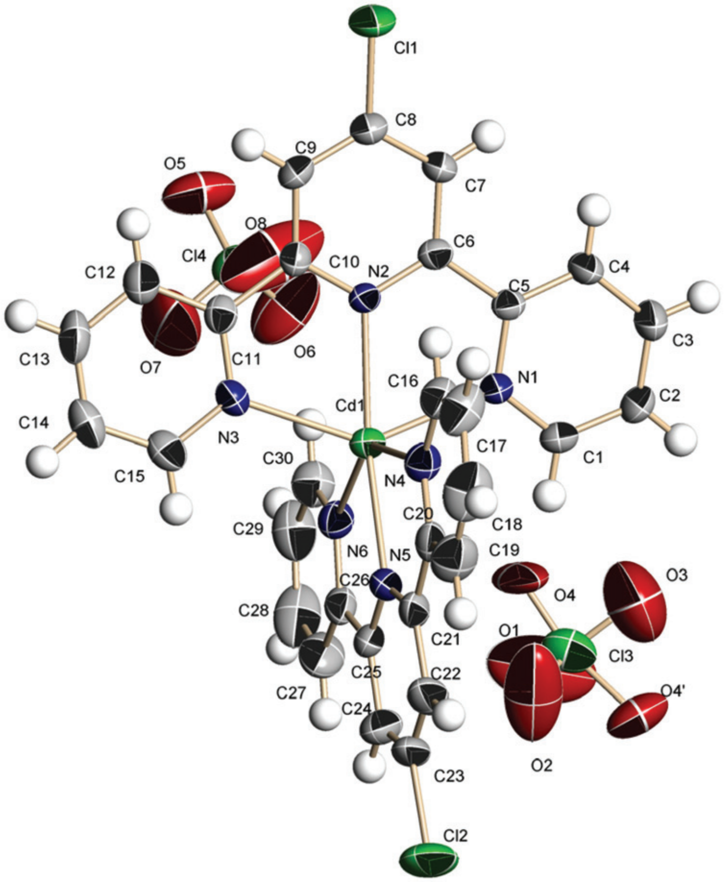

Figure 3. An ORTEP drawing of **2** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii.

3.2. *Single-crystal structures of $[Cd(tpyCl\text{-}\kappa^3N,N',N'')_2](ClO_4)_2$ (2), $[Zn(tpyCl\text{-}\kappa^3N,N',N'')_2](ClO_4)_2$ (3), and $[Zn(tpyCl\text{-}\kappa^3N,N',N'')_2](BF_4)_2$ (4)*

The atom-numbering schemes of **2**–**4** are shown in figures 3–5. In 1 : 2 Cd(II) complex, **2**, the Cd(II) center is coordinated by six nitrogens in a distorted octahedral coordination geometry. Four nitrogens (N1, N2, N3, and N5) from two tridentate tpyCl ligands constitute the basal plane with mean deviation from least-squares plane of 0.1355 Å, while the other two nitrogens (N4 and N6) from the same tpyCl ligand occupy the two apical positions with N6–Cd1–N4 bond angle of 140.5(2)°. All pyridine rings of tpyCl are essentially planar and the tpyCl ligands are perpendicular to each other with a dihedral angle of 90.4°. As for Zn(II) complex, **3**, the Zn(II) center is also coordinated by six nitrogens where four nitrogens (N2, N4, N5, and N6) from two tridentate tpyCl ligands constitute the basal plane with the mean deviation from least-squares plane of 0.0276 Å. The other two nitrogens (N1 and N3) from the same tpyCl ligand occupy two apical positions with the N1–Zn1–N3 bond angle of 151.5(4)°, exhibiting less distorted octahedral geometry. The dihedral angle between the two tpyCl ligands is 87.3°.

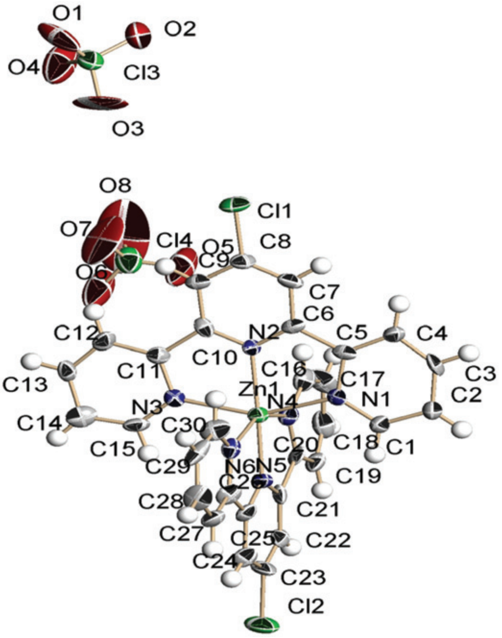

Figure 4. An ORTEP drawing of **3** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii.

Compounds **4** and **2** crystallize in the same centrosymmetric space group *P2₁/n* and have the same arrangement, although metal centers [Cd(II) or Zn(II)] and counterions [ClO_4^- or BF_4^-] are different. However, **3** crystallizes in a noncentrosymmetric space group *Cc*, even though it possesses ClO_4^- as **2** and the same central Zn(II) as **4**. The molecular structure of **4** is more analogous to that of **3** since the mean deviation from least-squares coordination plane is 0.0370 Å and the N6–Zn1–N4 bond angle is 150.9(2)°.

In the packing of **2**, π–π stacking interactions are found between each side ring of tpyCl and their contiguous counterparts with centroid–centroid separations of 3.729 and 3.732 Å, respectively. A 2-D π–π stacking structure is constructed and the 2-D framework is further packed into a 3-D structure with weak C–H ⋯ O hydrogen bonds between the pyridyl carbons (C4, C16, C18, and C24) and the perchlorate oxygens (O5, O7, O1, and O2) (figure 6). Similar 2-D π–π stacking structures are found between neighboring aromatic rings in **3** and **4** with different centroid–centroid separations of 3.680 and 3.746 Å in **3** and 3.639 and 3.678 Å in **4**. Moreover, C–H ⋯ Cl and C–H ⋯ O hydrogen bonds between pyridyl carbons and the chloride or perchlorate oxygens are found in **3** (figure 7), while C–H ⋯ Cl and C–H ⋯ F hydrogen bonds are observed in **4** [16, 28]. The 3-D supramolecular networks are also formed in **3** and **4**.

4. Conclusion

In this article, we reported two cadmium(II) and two zinc(II) complexes of tpyCl with 1 : 1 or 1 : 2 ratio of metal and ligand. The use of different counterions

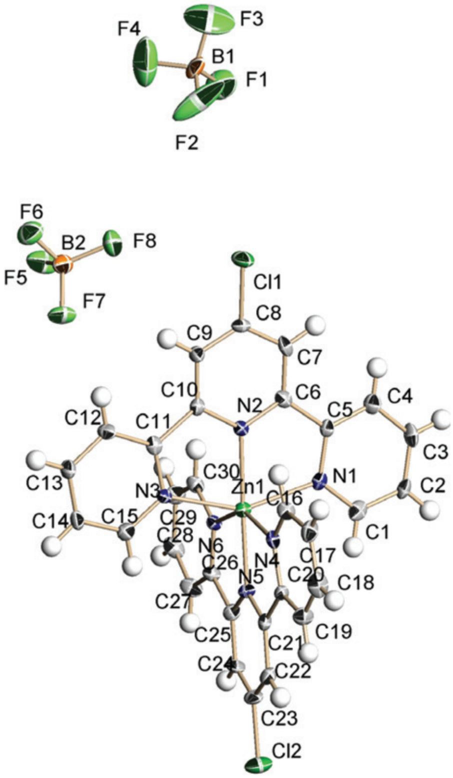

Figure 5. An ORTEP drawing of **4** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii.

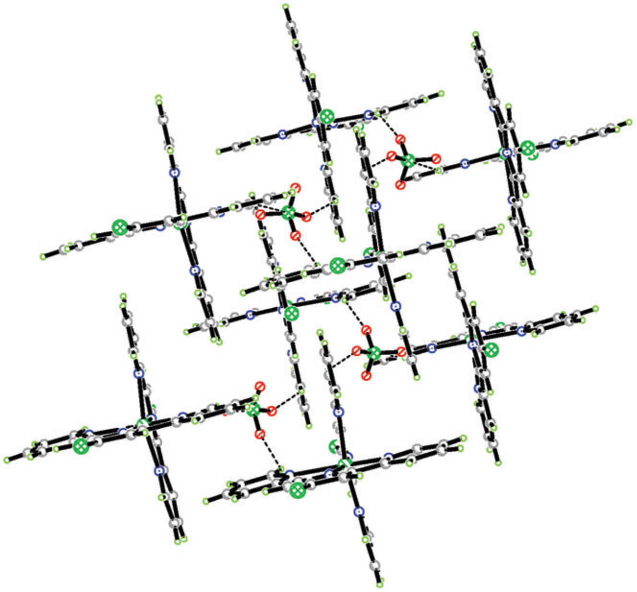

Figure 6. A perspective view of the supramolecular interactions in **2**.

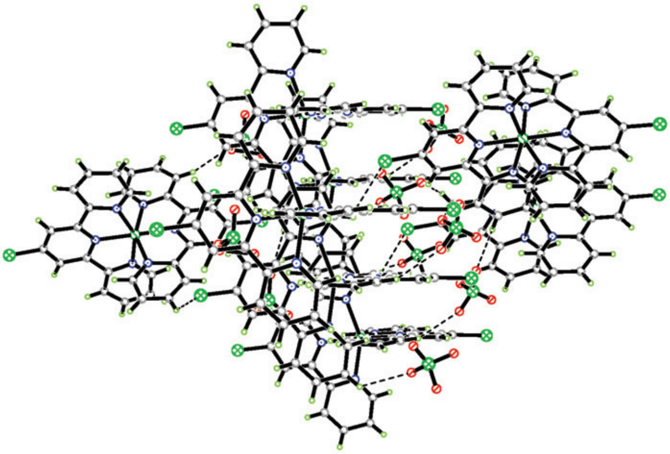

Figure 7. A perspective view of the supramolecular interactions in **3**.

(NO_3^-, ClO_4^-, and BF_4^-) may be responsible for the crystallographic symmetry and the formation of different frameworks of **1**–**4** [31]. Versatile supramolecular interactions including coordinative bonding, O–H···O, O–H···Cl, C–H···F, and C–H···Cl hydrogen bonding, and π–π stacking play essential roles in these cases.

Supplementary material

CCDC 696214–696217 contain the supplementary crystallographic data for **1**–**4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk

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