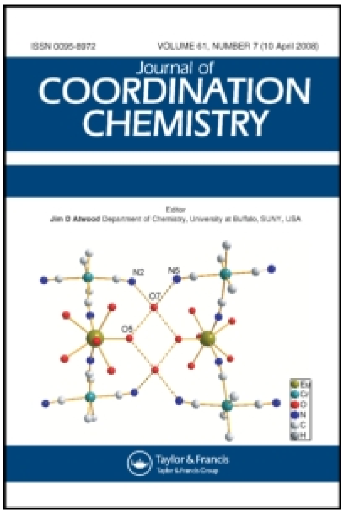

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Synthesis, crystal structures and toxicity of bicadmium(ii) complexes with macrocyclic, hexaaza-bearing, hydroxyethyl pendants

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SYNTHESIS, CRYSTAL STRUCTURES AND TOXICITY OF BICADMIUM(II) COMPLEXES WITH MACROCYCLIC, HEXAAZA-BEARING, HYDROXYETHYL PENDANTS

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Three bicadmium(II) complexes with hydroxyethyl pendants were synthesized by [2 + 2] Schiff-base condensation of 2-[bis(2-aminoethyl)amino]ethanol with sodium 2,6-diformyl-4-R-phenolate (for Complex **1**, R = F; Complex **2**, R = Cl; Complex **3**, R = CH_3) in the presence of Cd^{2+}. Crystals of **1** were monoclinic, space group $P2_1/c$, with $a = 16.251(9)$, $b = 21.424(11)$, $c = 12.994(7)$ Å and $\beta = 106.622(9)°$. Both Cd(II) atoms were hepta-coordinated with monocapped-octahedral geometry. Complex **3** crystals were isolated as triclinic, space group $P{-}1$ with $\alpha = 15.502(4)$, $b = 16.060(4)$, $c = 16.642(5)$ Å and $\alpha = 68.813(4)$, $\beta = 80.836(4)$, $\gamma = 86.551(4)°$. The coordination number and coordination geometry of the Cd ion in one cationic unit of **3** are similar to that of **1**, while in the other cationic unit, one Cd atom is N_3O_4 heptacoordinated and the other Cd atom has an N_3O_3 coordination environment and possesses a distorted octahedral geometry. The toxicity of these complexes was evaluated by testing antimicrobial activity against bacterial strands.

Keywords: Bicadmium(II) complex; Hydroxyethyl pendant; Crystal structure; Toxicity

INTRODUCTION

The study of pendant-arm macrocyclic complexes has been a very active area of research for many years because the ligating groups attaching to the macrocyclic skeleton can offer additional donor groups to maintain the coordination sphere of the metals and to modify the conformational, physical and chemical properties of macrocyclic complexes [1–3]. Cadmium(II) can inhibit RNA polymerase activity *in vivo*, and reacts readily with proteins and other biological molecules; long-term environmental exposure to cadmium can harm kidney function [4,5]. The study

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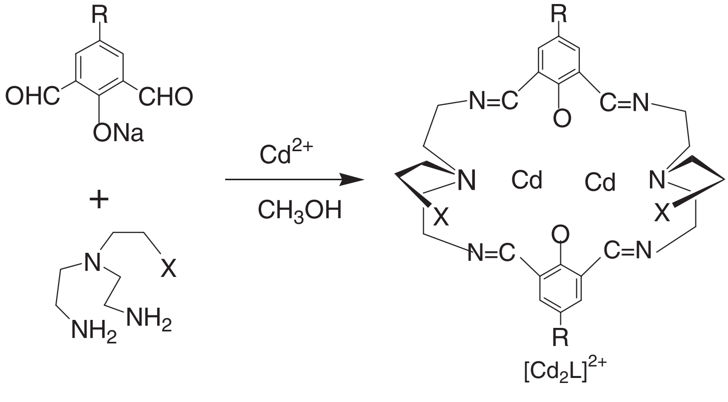

(in which when X = OH, R = F, Cl, CH_3 are corresponding to Cd_2L1, Cd_2L2, Cd_2L3, and when X = NH_2, R = Br, Cl, CH_3 are corresponding to Cd_2L1', Cd_2L2', Cd_2L3', respectively.)

of cadmium(II) complexes would be helpful in its toxicity research [6,7]. Recently, many new bicadmium(II) macrocyclic complexes involving functional pendants have been prepared and characterized [8–13], but few toxicity studies were reported on these complexes. Here we report the synthesis, structural characterization and toxicity of three new cadmium(II) macrocyclic complexes bearing hydroxyethyl pendants. The synthesis of these complexes is depicted in Scheme 1.

EXPERIMENTAL

Materials and Instrumentation

2-[Bis(2-aminoethyl)amino]ethanol was prepared according to the literature [14]. Sodium 2,6-diformyl-4-R-phenolates (sdrp) were prepared by the method described in the literature [15]. [Cd_2Ln']-bearing aminoethyl pendant arms were synthesized by [2 + 2] Schiff-base condensation of tris(2-aminoethyl)amine (tren) with sodium 2,6-diformyl-4-R-phenolate in the presence of Cd(II) (R = Br, L1′; R = Cl, L2′; R = CH_3, L3′) according to the literature [10]. All starting materials and solvents were of analytical purity.

Elemental analyses were determined with a Perkin Elmer 240c instrument. Solution electrical conductivities were measured by a BSD-A numerical conductometer (Jiangsu, China) with solution concentration of *ca* $1.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ in acetonitrile at 279 K. IR spectra were measured using KBr disks on a Nicolet 5DX FTIR spectrophotometer. ES mass spectral measurements of the complexes were carried out on an LCQ System (Finngann MAT, USA) using acetonitrile and methanol as the mobile phase.

Preparation of Metal Complexes

The complexes were synthesized by the following procedure. To a stirred solution of sdrp (0.5 mmol) and $Cd(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) in 20 cm^3 of absolute methanol was added dropwise a solution of 2-[bis(2-aminoethyl)amino]ethanol (0.5 mmol) in

TABLE I Analytical data for the complexes

Complex	*Yield (%)*	ΛM ($S\,cm^2\,mol^{-1}$)	*Empirical formula*	*Anal. found (calc.) (%)*		
				C	*H*	*N*
1	41	226	$C_{29}H_{39}N_6O_{14.50}F_2Cl_2Cd_2$	33.46 (33.55)	3.68 (3.76)	8.24 (8.10)
2	49	214	$C_{56}H_{74}N_{12}O_{27}Cl_8Cd_4$	31.96 (32.01)	3.69 (3.56)	8.21 (8.08)
3	51	211	$C_{60}H_{82}N_{12}O_{27}Cl_4Cd_4$	36.21 (36.09)	4.02 (4.11)	8.21 (8.42)

10 cm^3 of absolute methanol at 0°C. After stirring for 3 h at 45°C, yellowish microcrystals of the complexes [16] precipitated and were filtered off, washed with methanol and dried *in vacuo*. Yellowish single crystals of Complexes **1** and **3** suitable for X-ray structure determination were obtained by slow evaporation of the resulting filtrates for several days at ambient temperature. Table I lists analytical data for the complexes.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

X-ray Crystallography

Suitable crystals of Complexes **1** and **3** were mounted on glass fibers. The crystal data were collected at 293(2) K on a Bruker SMART/CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXL-97 and refined by full-matrix least-squares calculation on F^2 using SHELXL-97 [17]. All H atoms were placed in calculated positions. Full-matrix least-squares methods were used to refine an overall scale factor, positional and thermal parameters. The details of data collection, refinement and crystallographic data are summarized in Table II.

Antimicrobial Activity Determination

The toxicity of the complexes and $Cd(ClO_4)_2 \cdot 6H_2O$ was evaluated by testing antimicrobial activity to bacterial strands using the agar diffusion method as described in the literature [18,19]. Complexes and $Cd(ClO_4)_2 \cdot 6H_2O$ dissolved in DMF were tested against standard strains of *Candida albicans* CMCC (F) 98 001, *Staphylococcus aureus* CMCC (B) 26 003, *Bacillus pumilus* CMCC (B) 63 202 and *Klebosiella pneumoniae* CMCC (B) 46 117. Nutrient agar thawed by heating in a water bath was transferred to glass plates and frozen at about 37°C. After the test strains were spread on the solid nutrient agar surface, stainless-steel tubes (7.8 × 6 × 10 mm) were placed vertically on the surface. Samples (0.04 cm^3) of known concentration were injected into the steel tubes and allowed to incubate at 37°C for 24 h. The inhibition zone around the disk was calculated as the zone diameter in millimeters. Blank tests showed that DMF in the test solutions did not affect the test organisms. All tests were repeated three times and average data were taken as the final result.

TABLE II Crystal data, data collection and structure refinement parameters for Complexes **1** and **3**

Complex	**1**	**3**
Empirical formula	$C_{29}H_{39}N_6O_{14.50}F_2Cl_2Cd_2$	$C_{60}H_{82}N_{12}O_{27}Cl_4Cd_4$
Formula weight	1037.36	1994.87
Radiation (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P{-}1$
a (Å)	16.251(9)	15.502(4)
b (Å)	21.424(11)	16.060(4)
c (Å)	12.994(7)	16.642(5)
α (°)	90	68.813(4)
β (°)	106.622(9)	80.836(4)
γ (°)	90	86.551(4)
V (Å^3)	4335(4)	3813.8(18)
Z	4	2
D_{calcd} (Mg m^{-3})	1.589	1.893
Absorption coefficient (mm^{-1})	1.178	3.659
θ range (°)	2.55 to 25.01	1.33 to 26.40
Index ranges	$-14 \le h \le 19$; $-25 \le k \le 23$; $-15 \le l \le 15$	$-19 \le h \le 16$; $-19 \le k \le 20$; $-20 \le l \le 20$
Reflections collected	21 261	21 796
Independent reflections	7521 [$R_{\mathrm{int}} = 0.1178$]	15 278 [$R_{\mathrm{int}} = 0.0193$]
Independent reflections (> 2σ)	3178	11 348
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents
Max/min transmissions	1.000 000 and 0.619 065	1.000 000 and 0.819 637
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7521/261/624	15 278/625/1115
Goodness-of-fit on F^2	1.039	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0750$, $wR_2 = 0.1577$	$R_1 = 0.0670$, $wR_2 = 0.2131$
R indices (all data)	$R_1 = 0.1914$, $wR_2 = 0.2105$	$R_1 = 0.0934$, $wR_2 = 0.2424$
Largest diff. peak and hole	0.900 and −1.035 e Å^{-3}	2.084 and −1.319 e Å^{-3}

RESULTS AND DISCUSSION

Crystal Structures

The crystal structure of Complex **1** consists of a cationic unit of $[Cd_2L1]^{2+}$, coordinated water molecules and noncoordinated perchlorate ions. A perspective view of $[Cd_2L1]^{2+}$ is shown in Fig. 1. Selected bond lengths and angles relevant to the Cd coordination sphere are listed in Table III. Both Cd(II) atoms are heptacoordinated with mono-capped-octahedral geometry by three N atoms, one O atom of the hydroxyethyl pendant, one O atom of water and two phenoxy oxygen atoms serving as bridging groups. Two hydroxyethyl arms are located on the same side of the plane defined by the macrocyclic ligand. The dihedral angle of the two aromatic rings is 70.5°, with centroid–centroid distance 7.867 Å. The long Cd(1)–Cd(2) distance of 3.502 Å indicates that there is no interaction between the two metal atoms. Cd–O (phenoxy oxygen) distances are in the range 2.28–2.35 Å; normal coordination bonds. The Cd–N (imino) distances are in the range 2.27–2.616 Å, shorter than the Cd–N (bridgehead) distance 2.592–2.556 Å, implying a weaker interaction between Cd and bridgehead nitrogen atoms than Cd and imino atoms. Comparing $[Cd_2L1]$ with the analogous complex $[Cd_2L1']$, derived from condensation of tren and sodium 2,6-diformyl-4-bromophenolate in the presence of Cd(II) ion reported previously by Xu *et al.* [10], the important differences lie in the coordination geometry and the strength of

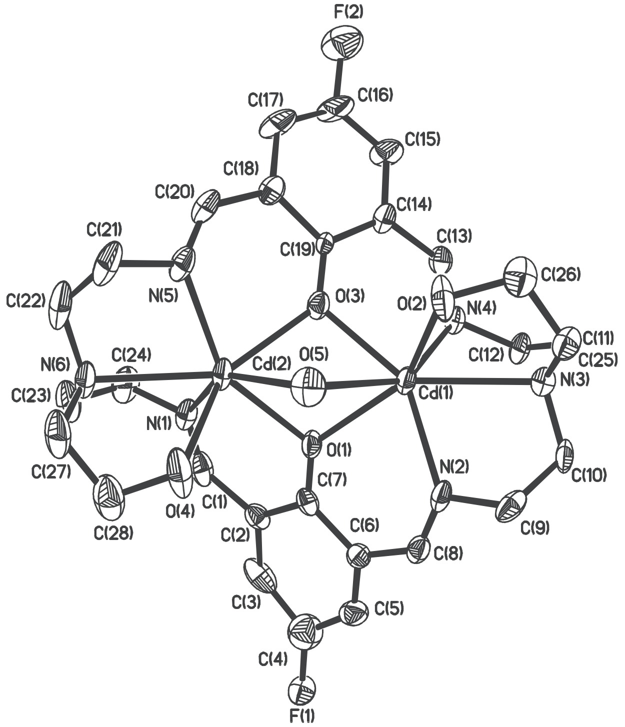

FIGURE 1 Perspective view of $[Cd_2L1]^{2+}$ with the atom numbering scheme (ellipsoids at 30% probability).

TABLE III Selected bond distances (Å) and angles (°) for $[Cd_2L1]$

Cd(1)–N(4)	2.272(10)	Cd(2)–N(1)	2.280(13)
Cd(1)–N(2)	2.293(11)	Cd(2)–N(5)	2.281(13)
Cd(1)–O(3)	2.296(8)	Cd(2)–O(1)	2.283(8)
Cd(1)–O(1)	2.348(8)	Cd(2)–O(3)	2.316(8)
Cd(1)–O(2)	2.399(10)	Cd(2)–O(4)	2.377(11)
Cd(1)–N(3)	2.592(10)	Cd(2)–O(5)	2.610(10)
Cd(1)–O(5)	2.611(10)	Cd(2)–N(6)	2.616(10)
N(4)–Cd(1)–N(2)	117.4(4)	N(1)–Cd(2)–N(5)	116.2(4)
N(4)–Cd(1)–O(3)	78.6(3)	N(1)–Cd(2)–O(1)	78.1(3)
N(2)–Cd(1)–O(3)	147.1(4)	N(5)–Cd(2)–O(1)	149.2(4)
N(4)–Cd(1)–O(1)	111.6(3)	N(1)–Cd(2)–O(3)	108.4(3)
N(2)–Cd(1)–O(1)	75.8(4)	N(5)–Cd(2)–O(3)	77.2(4)
O(3)–Cd(1)–O(1)	71.4(3)	O(1)–Cd(2)–O(3)	72.3(3)
N(4)–Cd(1)–O(2)	95.2(4)	N(1)–Cd(2)–O(4)	96.0(4)
N(2)–Cd(1)–O(2)	115.7(4)	N(5)–Cd(2)–O(4)	116.8(5)
O(3)–Cd(1)–O(2)	89.3(3)	O(1)–Cd(2)–O(4)	86.5(4)
O(1)–Cd(1)–O(2)	142.2(3)	O(3)–Cd(2)–O(4)	142.9(3)
N(4)–Cd(1)–N(3)	70.2(3)	N(1)–Cd(2)–O(5)	149.3(4)
N(2)–Cd(1)–N(3)	72.4(4)	N(5)–Cd(2)–O(5)	94.2(4)
O(3)–Cd(1)–N(3)	139.6(3)	O(1)–Cd(2)–O(5)	73.1(3)
O(1)–Cd(1)–N(3)	144.0(3)	O(3)–Cd(2)–O(5)	72.8(3)
O(2)–Cd(1)–N(3)	69.3(3)	O(4)–Cd(2)–O(5)	72.1(4)
N(4)–Cd(1)–O(5)	148.5(4)	N(1)–Cd(2)–N(6)	69.2(4)
N(2)–Cd(1)–O(5)	94.0(4)	N(5)–Cd(2)–N(6)	73.6(4)
O(3)–Cd(1)–O(5)	73.1(3)	O(1)–Cd(2)–N(6)	136.4(4)
O(1)–Cd(1)–O(5)	72.1(3)	O(3)–Cd(2)–N(6)	145.0(4)
O(2)–Cd(1)–O(5)	71.3(3)	O(4)–Cd(2)–N(6)	69.6(4)
N(3)–Cd(1)–O(5)	126.2(3)	O(5)–Cd(2)–N(6)	127.7(4)

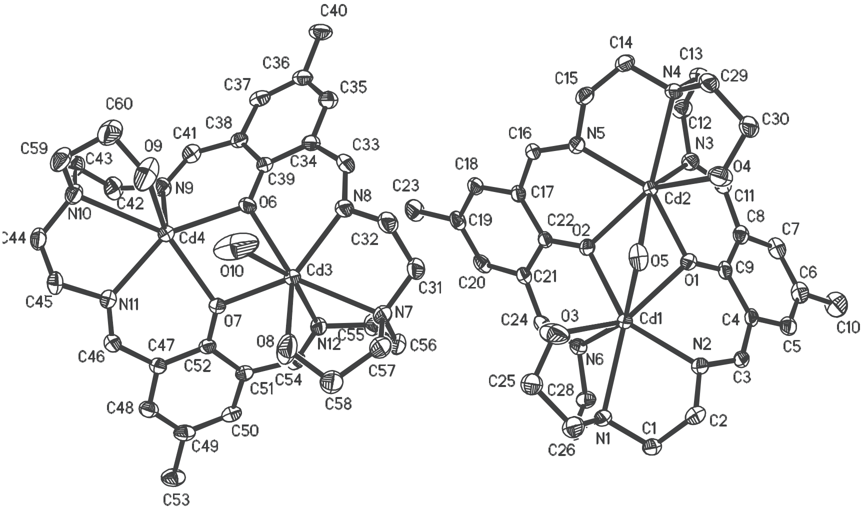

FIGURE 2 Perspective view of $[Cd_2L3]^{2+}$ with the atom numbering scheme (ellipsoids at 30% probability).

coordination. Each Cd(II) in [Cd_2L1'] lies in an N_4O_2 coordination environment, which takes the form of a capped trigonal bipyramid, and Cd–O or Cd–N bond distances are shorter than the corresponding distances in [Cd_2L1]. Such differences are attributed to the pendant arm and substituting group.

Compared to Complex **1**, the crystal structure of **3** is quite different. Complex **3** consists of two cationic units, coordinated water molecules and noncoordinated perchlorate ions. The perspective view of $[Cd_2L3]^{2+}$ is shown in Fig. 2; selected bond lengths and angles relevant to the Cd coordination sphere are listed in Table IV. Two dinuclear cations, ${[Cd_2L3]_A}^{2+}$ and ${[Cd_2L3]_B}^{2+}$, joined together through intermolecular van der Waals forces with both pendant arms being forced to point toward one side of the macrocycle. ${[Cd_2L3]_A}^{2+}$ is basically similar to $[Cd_2L1]^{2+}$, differing with respect to bond lengths and angles. In ${[Cd_2L3]_B}^{2+}$, Cd(3) is N_3O_4 heptacoordinated with monocapped-octahedral geometry. Cd(4) lies in an N_3O_3 coordination environment and possesses a distorted octahedral geometry. The dihedral angles of the two aromatic rings is 101.4°, with centroid–centroid distance 7.647 Å, very similar to the two rings in ${[Cd_2L3]_A}^{2+}$ (92.2°, 7.397 Å). The distance between Cd(4) and O(10) is 3.157 Å, too long to be coordinated. The most distinct difference for ${[Cd_2L3]_A}^{2+}$ *vs.* ${[Cd_2L3]_B}^{2+}$ is that O(5) in coordinating water in the former is bridged with Cd(1) and Cd(2), but O(10) in the latter is only coordinated with Cd(3). In $[Cd_2L1]^{2+}$, there is only one kind of cationic unit, in which coordinating water is bridged with Cd(1) and Cd(2). This difference between $[Cd_2L1]^{2+}$ and $[Cd_2L3]^{2+}$ may be attributed to the influence of the substituting group.

Spectral Characteristics

The IR and ES-MS spectra of the three complexes resemble each other indicating a similar structural relationship (Table V). Condensation of all primary amine groups and carbonyl groups is confirmed by the lack of N–H double stretching bands in the IR region 3150–3450 cm^{-1} and the presence of strong C=N stretching

TABLE IV Selected bond distances (Å) and angles (°) for [Cd_2L3]

Cd(1)–O(1)	2.387(4)	Cd(3)–O(6)	2.376(4)
Cd(1)–O(2)	2.261(4)	Cd(3)–O(7)	2.301(4)
Cd(1)–O(3)	2.419(5)	Cd(3)–O(8)	2.403(5)
Cd(1)–O(5)	2.493(5)	Cd(3)–O(10)	2.485(6)
Cd(1)–N(1)	2.570(5)	Cd(3)–N(7)	2.604(5)
Cd(1)–N(2)	2.282(5)	Cd(3)–N(8)	2.286(5)
Cd(1)–N(6)	2.288(5)	Cd(3)–N(12)	2.275(5)
Cd(2)–O(1)	2.255(4)	Cd(4)–O(6)	2.275(4)
Cd(2)–O(2)	2.354(4)	Cd(4)–O(7)	2.322(4)
Cd(2)–O(4)	2.384(5)	Cd(4)–O(9)	2.314(5)
Cd(2)–O(5)	2.576(5)	Cd(4)–N(9)	2.267(5)
Cd(2)–N(3)	2.280(5)	Cd(4)–N(10)	2.632(5)
Cd(2)–N(4)	2.571(4)	Cd(4)–N(11)	2.268(5)
Cd(2)–N(5)	2.270(4)		
O(2)–Cd(1)–N(2)	146.48(15)	N(12)–Cd(3)–N(8)	115.42(18)
O(2)–Cd(1)–N(6)	79.07(15)	N(12)–Cd(3)–O(7)	78.80(15)
N(2)–Cd(1)–N(6)	112.99(16)	N(8)–Cd(3)–O(7)	148.31(15)
O(2)–Cd(1)–O(1)	71.99(13)	N(12)–Cd(3)–O(6)	110.64(16)
N(2)–Cd(1)–O(1)	74.55(15)	N(8)–Cd(3)–O(6)	76.55(15)
N(6)–Cd(1)–O(1)	113.09(16)	O(7)–Cd(3)–O(6)	71.85(13)
O(2)–Cd(1)–O(3)	87.54(18)	N(12)–Cd(3)–O(8)	95.8(2)
N(2)–Cd(1)–O(3)	121.1(2)	N(8)–Cd(3)–O(8)	116.7(2)
N(6)–Cd(1)–O(3)	93.5(2)	O(7)–Cd(3)–O(8)	87.93(18)
O(1)–Cd(1)–O(3)	141.67(15)	O(6)–Cd(3)–O(8)	142.04(16)
O(2)–Cd(1)–O(5)	73.28(15)	N(12)–Cd(3)–O(10)	158.8(2)
N(2)–Cd(1)–O(5)	97.83(16)	N(8)–Cd(3)–O(10)	85.7(3)
N(6)–Cd(1)–O(5)	149.03(16)	O(7)–Cd(3)–O10	83.8(3)
O(1)–Cd(1)–O(5)	71.26(14)	O(6)–Cd(3)–O(10)	74.7(2)
O(3)–Cd(1)–O(5)	71.94(18)	O(8)–Cd(3)–O(10)	71.4(2)
O(2)–Cd(1)–N(1)	139.77(14)	N(12)–Cd(3)–N(7)	70.94(17)
N(2)–Cd(1)–N(1)	72.40(15)	N(8)–Cd(3)–N(7)	72.30(16)
N(6)–Cd(1)–N(1)	71.93(16)	O(7)–Cd(3)–N(7)	138.60(14)
O(1)–Cd(1)–N(1)	145.44(13)	O(6)–Cd(3)–N(7)	145.35(14)
O(3)–Cd(1)–N(1)	67.48(16)	O(8)–Cd(3)–N(7)	68.27(16)
O(5)–Cd(1)–N(1)	123.04(16)	O(10)–Cd(3)–N(7)	117.0(3)
O(1)–Cd(2)–N(5)	148.68(15)	N(9)–Cd(4)–N(11)	115.92(18)
O(1)–Cd(2)–N(3)	80.11(15)	N(9)–Cd(4)–O(6)	79.86(16)
N(5)–Cd(2)–N(3)	114.31(17)	N(11)–Cd(4)–O(6)	150.84(15)
O(1)–Cd(2)–O(2)	72.74(13)	N(9)–Cd(4)–O(9)	104.6(2)
N(5)–Cd(2)–O(2)	76.10(14)	N(11)–Cd(4)–O(9)	106.3(2)
N(3)–Cd(2)–O(2)	110.39(16)	O(6)–Cd(4)–O(9)	91.83(19)
O(1)–Cd(2)–O(4)	86.96(17)	N(9)–Cd(4)–O(7)	114.94(16)
N(5)–Cd(2)–O(4)	116.12(18)	N(11)–Cd(4)–O(7)	77.69(15)
N(3)–Cd(2)–O(4)	98.62(19)	O(6)–Cd(4)–O(7)	73.31(13)
O(2)–Cd(2)–O(4)	140.43(15)	O(9)–Cd(4)–O(7)	133.75(19)
O(1)–Cd(2)–N(4)	138.27(14)	N(9)–Cd(4)–N(10)	70.17(17)
N(5)–Cd(2)–N(4)	72.68(15)	N(11)–Cd(4)–N(10)	71.60(17)
N(3)–Cd(2)–N(4)	71.90(16)	O(6)–Cd(4)–N(10)	137.35(15)
O(2)–Cd(2)–N(4)	146.06(13)	O(9)–Cd(4)–N(10)	68.22(17)
O(4)–Cd(2)–N(4)	67.93(15)	O(7)–Cd(4)–N(10)	147.07(14)
O(1)–Cd(2)–O(5)	71.80(15)	N(4)–Cd(2)–O(5)	124.98(15)
N(5)–Cd(2)–O(5)	94.84(16)	O(2)–Cd(2)–O(5)	70.28(14)
N(3)–Cd(2)–O(5)	150.39(16)	O(4)–Cd(2)–O(5)	71.22(17)

bands at 1642–1645 cm^{-1}. The presence of a broad band at 3350–3420 cm^{-1} is characteristic of an OH group of pendant arms. The strong peaks at 1082–1115 cm^{-1} without splitting show that ClO_4^- does not coordinate with Cd. The main peaks at *m*/*z* 781.0 and 391 in Complex **1** are assigned to [Cd_2L1_{-H}]$^+$ and [Cd_2L1]$^{2+}$, respectively. Similarly, the peaks at *m*/*z* 813.1 and 407.1 in Complex **2** correspond to [Cd_2L2_{-H}]$^+$ and

TABLE V IR and ES-MS spectra

Complex	*ν(OH)*	*ν(CH)*	*ν(C=N)*	*ν(ClO$_4$)*	*m/z (%)*	
					$[Cd_2L_{-H}]^+$	*$[Cd_2L]^{2+}$*
1	3352	2857, 2900	1642	1103	781.0 (40%)	391.1 (100%)
2	3350	2856, 2900	1643	1115	813.1 (14%)	407.1 (100%)
3	3401	2849, 2889	1645	1082	773.1 (100%)	387.2 (26%)

TABLE VI The diameter of inhibition zone (mm)

Compound	*Conc. of complex (mg cm^{-3})*	*Diameter of inhibition zone (mm)*			
		Candida albicans	*Staphylococcus aureus*	*Bacillus pumilus*	*Klebosiella pneumoniae*
$[Cd_2L1]$	10.0	19.8 (18.3)	41.3 (36.2)	25.6 (22.5)	23.5 (21.4)
($[Cd_2L1']$)	5.0	17.2 (17.2)	36.8 (33.8)	21.5 (20.8)	20.6 (18.7)
	2.5	15.9 (15.3)	33.1 (32.1)	17.8 (18.5)	17.8 (15.9)
	1.3	12.5 (12.2)	30.5 (28.9)	15.6 (13.2)	15.3 (13.1)
$[Cd_2L2]$	10.0	18.9 (18.1)	40.1 (35.1)	22.2 (22.6)	22.3 (20.9)
($[Cd_2L2']$)	5.0	17.5 (16.9)	36.2 (33.2)	20.4 (20.1)	19.0 (18.3)
	2.5	15.3 (15.0)	34.2 (30.5)	16.0 (17.3)	16.1 (15.6)
	1.3	12.1 (12.0)	32.4 (27.6)	13.3 (11.6)	13.1 (12.9)
$[Cd_2L3]$	10.0	19.2 (17.8)	40.9 (34.1)	23.4 (21.6)	22.7 (20.0)
($[Cd_2L3']$)	5.0	16.4 (15.7)	37.1 (32.1)	21.2 (17.8)	19.0 (17.9)
	2.5	14.5 (13.1)	36.2 (31.7)	15.6 (16.5)	14.8 (15.9)
	1.3	12.2 (11.4)	34.0 (28.8)	13.4 (12.5)	13.3 (12.8)
$Cd(ClO_4)_2$	14.0	19.4	38.6	21.7	19.0
	7.0	18.6	34.1	19.4	15.0
	3.5	11.7	31.9	17.5	13.1
	1.8	10.3	29.6	15.4	11.0

(Values of the toxicity (parentheses) of the similar bicadmium complexes $[Cd_2Ln']$ are shown for comparison.)

$[Cd_2L2]^{2+}$; peaks at *m/z* 773.1 and 387.2 in Complex **3** correspond to $[Cd_2L3_{-H}]^+$ and $[Cd_2L3]^{2+}$. All the species were confirmed by good agreement between the observed and calculated isotopic distribution.

Antimicrobial Activity

$Cd(ClO_4)_2 \cdot 6H_2O$ and the complexes were active against four test organisms, showing similar antimicrobial activities (Table VI). The highest antimicrobial activity among the group of these organisms was observed against *Staphylococcus aureus*. In the range of 14–1.3 mg ml^{-1}, these compounds were active against the test strains with increase of concentration. The substituting group had little influence on antimicrobial activity, but a small difference in toxicity between $[Cd_2Ln]$ and $[Cd_2Ln']$ was observed, probably due to the different pendant arms. Theoretically, the formation of a complex can reduce the toxicity of Cd, but unexpectedly, all the tested complexes had higher antimicrobial activities than $Cd(ClO_4)_2 \cdot 6H_2O$. Further study is in progress.

Supplementary Material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC 227 938 for complex [Cd_2L1] and CCDC 227 937 for [Cd_2L3]. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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References

[1] K.P. Wainwright, *Coord. Chem. Rev.* **166**, 35 (1997).
[2] G.A. McLachlan, S.J. Brudenell, G.D. Fallon, R.L. Martin, L. Spiccia and E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.* 439 (1995).
[3] S.A. Li, D.F. Li, D.X. Yang, Y.Z. Li, J. Huang, K.B. Yu and W.X. Tang, *J. Chem. Soc., Chem. Commun.* 1 (1995).
[4] K.B. Jacobson and J.E. Turner, *Toxicology* **60**, 1 (1980).
[5] M. Trzcinka-Ochocka, M. Jakubowski, G. Razniewska, T. Halatek and A. Gazewski, *Environ. Res.* **95**, 119 (2004).
[6] M. Dakanali, E.T. Kefalas, C.P. Raptopoulou, A. Terzis, T. Mavromoustakos and A. Salifoglou, *Inorg. Chem.* **42**, 2531 (2003).
[7] S.C. Jose, E.C. Eduardo, D.C. Maria, S. Agustin, S. Jose, M.V. Jose and Z.S. Julio, *Inorg. Chem.* **34**, 2430 (1995).
[8] X.Y. Xu, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *J. Coord. Chem.* **42**, 25 (1997).
[9] X.Y. Xu, Z.L. Wang, Q.H. Luo, M.C. Shen, N.X. Zhang, X.G. Zhou and Z.Y. Zhou, *J. Coord. Chem.* **43**, 81 (1998).
[10] X.Y. Xu, Z.L. Wang, Q.H. Luo, M.C. Shen, N.X. Zhang, X.G. Zhou and Z.Y. Zhou, *J. Coord. Chem.* **43**, 281 (1998).
[11] X.Y. Xu, W.X. Ma, H. Cheng, W.W. Liu, M.X. Zhang, Q.L. Liu and Z.D. Zhang, *J. Coord. Chem.* **48**, 1 (1999).
[12] X.Y. Xu, J.L. Cheng, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *Polyhedron* **16**, 223 (1996).
[13] J. Wang, X.Y. Xu, J.L. Cheng, Q.H. Luo, M.C. Shen, X.Y. Huang and Q.J. Wu, *Inorg. Chim. Acta* **256**, 121 (1997).
[14] S. Bin, R. Jenny, O. Christian, F.E. Hahn, L. Thomas and O. Chris, *Inorg. Chem.* **40**, 1527 (2001).
[15] S. Taniguch, *Bull. Chem. Soc. Jpn* **57**, 268 (1984).
[16] The structure of Complex **2** has been accepted by *Chinese J. Struct. Chem.* (only brief comments in the text).
[17] G.M. Sheldrick, SHELXL-97, *Program for the Refinement of Crystal Structures* (University of Göttingen, Germany) (1997).
[18] K.S. Lv, Y.C. Xu, H. Yu and Y. Shi, *Environ. Monitor. China* **7**, 9 (1991).
[19] N. Raman, A. Kulandaisamy and K. Jeyasubramanian, *Synth. React. Inorg. Met.-Org. Chem.* **32**, 1583 (2002).