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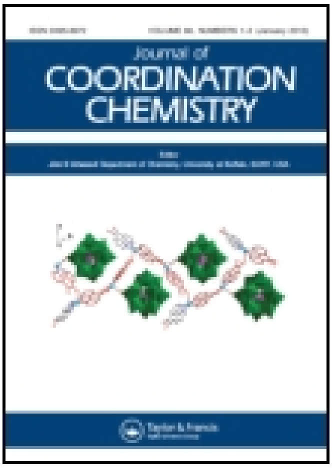

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Coordination chemistry of a mono-dibenzofuran derivative of 1,4,7,10-tetraazacyclododecane

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Coordination chemistry of a mono-dibenzofuran derivative of 1,4,7,10-tetraazacyclododecane

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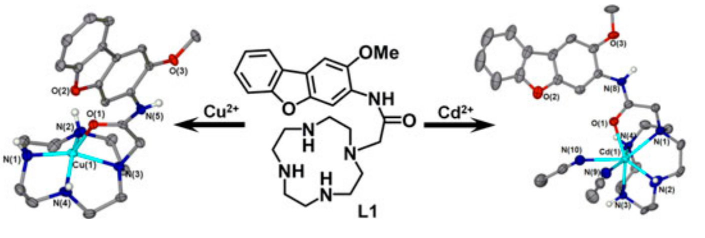

Copper(II) and cadmium(II) complex of a mono-dibenzofuran derivative of 1,4,7,10-tetraazacyclododecane (cyclen), **L1**, have been prepared by reaction of the mono-dibenzofuran-substituted cyclen with either copper(II) or cadmium(II) perchlorate in acetonitrile. This yielded the corresponding divalent metal complexes, $[Cu(\mathbf{L1})](ClO_4)_2\cdot H_2O$ (**C1**) and $[Cd(\mathbf{L1})](ClO_4)_2\cdot H_2O$ (**C2**), which were isolated as single crystals suitable for X-ray crystallography by diffusing diethyl ether into an acetonitrile solution of each complex. For the copper(II) complex, **C1**, the X-ray crystal structure revealed a distorted square pyramidal Cu(II) coordination sphere occupied by four amine nitrogens from the cyclen ring and one oxygen from the amide linkage present in **L1**. On the other hand, the metal center in the cadmium complex is seven coordinate, with two weakly bound acetonitrile molecules occupying two additional coordination sites about the Cd(II) center; these bind *cis* to the amide oxygen. The coordination geometry is best described as monocapped trigonal prismatic. In both complexes, the secondary amine nitrogens on the cyclen macrocycle form hydrogen bonds with perchlorate counterions present in the crystal lattice. Titration of **L1** with various metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) in acetonitrile revealed a gradual quenching of the benzofuran emission with increasing $[M^{2+}]$ consistent with formation of metal complexes with a 1 : 1 M^{2+} : **L1** stoichiometry. From the emission data, the conditional stability constant was determined to be 10–20 times higher for the Cu(II) complex than the other divalent metal complexes investigated.

Keywords: Coordination chemistry; Macrocyclic ligands; Crystal structures; Fluorescence; Metal ion-binding affinity

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1. Introduction

The use of macrocycles as chelating agents for metal ions is an ongoing area of research due, in part, to the wide range of biomedical applications for metal complexes and metal ion complexing agents, including as fluorescent sensors and neuroimaging agents [1–5]. Synthesis of fluorescent sensors for the detection and quantification of a wide variety of substances represents a growing field in chemistry [6–14]. Macrocycles represent particularly attractive scaffolds for the development of sensors for both metal ions and metal ion-coordinating analytes because of the ease with which they may be elaborated synthetically to incorporate fluorescent moieties as well as tune their coordination properties. Amongst the many examples of macrocycle-based fluorescent sensors that have been reported in the literature [8, 15–18], 1,4,7,10-tetraazacyclododecane (cyclen)-based derivatives feature prominently due to the ability of cyclen to form very stable metal complexes with a range of metal ions, whilst at the same time leaving coordination sites available for potential interaction with additional ligands (analytes), such as biologically important molecules [19, 20].

Benzofuran is a fluorescent molecule that has attracted the attention of researchers because of its ability to bind to the amyloid plaques formed during Alzheimer's disease [21–23]. Indeed, derivatives of benzofuran derivatives exhibit similar activity to chrysamine G, Congo red, and Thioflavin-T derivatives [21–23]. Synthetic protocols have also been developed to label some of these with positron emitters such as ^{11}C and ^{18}F that can be subsequently used for imaging via positron emission tomography (PET) [24–26]. An alternative approach would be the introduction of benzofuran as a pendant arm on a macrocycle, such as cyclen. This would allow the use of the benzofuran as an amyloid plaque-binding agent and fluorescent probe as well as providing for the possibility of introducing additional imaging capability in the form of a radiometal ion, such as $^{64}Cu^{2+}$ [27].

As a part of ongoing investigations into the design and synthesis of novel imaging agents, we recently reported the synthesis of two dibenzofuran-cyclen derivatives by functionalization of one or two cyclen secondary amines [27]. Fluorescence studies revealed that emission from one of the ligands was completely quenched by the addition of Cu^{2+} ions, but only partially by Zn^{2+} ions, a somewhat surprising result, as the binding of Zn^{2+} ions commonly increases the fluorescent emission of a wide variety of ligands bearing fluorophores [3, 16]. In this article, we report the synthesis, characterization, and X-ray crystal structures of copper(II) and cadmium(II) complexes of the mono-dibenzofuran-substituted cyclen ligand **L1** and reveal a relatively uncommon seven-coordinate metal geometry for the cadmium(II) complex. In addition, we have investigated the in-solution fluorescence characteristics of the ligand in the presence of a variety of metal ions and have estimated the conditional metal-binding constants and stoichiometry for metal ion complexation.

2. Experimental

2.1. *Materials and methods*

All chemicals were purchased from Sigma-Aldrich and used without purification. Unless otherwise stated, each reaction was conducted under nitrogen. Column chromatography was performed using silica gel (60 mesh) from Merck. The solvent used for elution varied depending on the compound of interest. The mono-dibenzofuran-substituted cyclen derivative (**L1**) was prepared by a published method [27].

2.2. *Spectroscopic studies*

^{1}H and ^{13}C NMR spectra were recorded on either 300 or 400 MHz (Bruker or Varian) spectrometers using either $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported as δ values in parts per million (ppm). Splitting patterns were designated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer, fitted with an ATR platform, at a resolution of 4 cm^{-1}. Mass spectra were obtained using a Micromass Platform II quadrupole mass spectrometer fitted with an electrospray source. Microanalyses were performed by the Campbell Microanalytical Service, University of Otago, New Zealand. Electronic and fluorescence spectra were recorded at room temperature on a Cary 5G UV–vis-NIR and Varian Cary Eclipse fluorescence spectrophotometer, respectively, using 1 cm quartz cuvettes and acetonitrile as solvent. For the fluorescence measurements, the wavelength of excitation and slit width were set at 300 and 5 nm, respectively, and the fluorescence emission was measured from 310 to 550 nm with a slit width of 5 nm. Copper(II), cadmium(II), cobalt(II), nickel(II), and manganese(II) perchlorate salts were used as metal ion sources. The titration was performed by adding known volumes of a 10 mM acetonitrile solution of each metal salt to 3 mL of a 33.3 μM solution of the trifluoroacetate salt of **L1** in acetonitrile, giving a final metal concentration in the range 0–66.7 μM. Fitting of the fluorescence data to obtain the conditional equilibrium constants and the stoichiometry of the complexes was performed using the program Origin by least-square analysis.

2.3. *Synthesis of complexes*

2.3.1. [Cu(L1)]$(ClO_4)_2\cdot H_2O$ (C1). A copper(II) solution, prepared by dissolving Cu$(ClO_4)_2\cdot 6H_2O$ (45 mg, 0.12 mM) in 1 mL of acetonitrile, was added to a solution of **L1** (50 mg, 0.12 mM) dissolved in 1 mL of acetonitrile, resulting in formation of a dark blue solution. Diffusion of diethyl ether into this solution afforded dark blue crystals of **C1** suitable for X-ray crystallography. Yield: 46 mg (54%).

Analytical Data IR spectrum (ATR): ν 3534br m, 3269vs, 2885m, 2840m, 1643s, 1539s, 1470s, 1068vs, 963m, 862w, 620w cm^{-1}. Elemental analysis: Calcd for $C_{23}H_{31}CuCl_2N_5O_{11}\cdot H_2O$ (%): C, 39.1; H, 4.7; N, 9.9. Found: C, 38.8; H, 4.5; N, 10.2. ESI MS (+ mode): 488.0 $[M\text{–}H\text{–}2ClO_4]^+$, 244.1 $[M\text{–}2ClO_4]^{2+}$. UV–vis: 590 nm ($\varepsilon = 275\ M^{-1}\ cm^{-1}$).

2.3.2. [Cd(L1)]$(ClO_4)_2\cdot H_2O$ (C2). The cadmium complex of **L1** was prepared in the same manner as **C1** but using $Cd(ClO_4)_2\cdot 6H_2O$ (50 mg, 0.12 mM) and **L1** (50 mg, 0.12 mM). Yield: 43 mg (44%). Crystals suitable for X-ray crystallography, obtained by diffusing diethyl ether into the acetonitrile solution of **C2**, were shown to have two weakly coordinated acetonitrile molecules and the composition [Cd(**L1**)$(CH_3CN)_2](ClO_4)_2$ (**C2′**, *vide infra*).

Analytical Data IR spectrum (ATR): ν 3307vs, 2965sh, 2913m, 2868m, 1633m, 1536s, 1470m, 1453m, 1429m, 1085vs, 1031vs, 925m, 844w, 759w, 619w cm^{-1}. Elemental analysis: Calcd for $C_{23}H_{31}CdCl_2N_5O_{11}\cdot H_2O$ (%): C, 36.6; H, 4.4; N, 9.3. Found: C, 36.6; H, 4.1; N, 9.2. ESI MS (+ mode): 637.8 $[M\text{–}ClO_4]^+$, 269.4 $[M\text{–}2ClO_4]^{2+}$.

2.4. *Crystal and structure refinement data*

Single crystals were mounted on thin glass fibers. X-ray crystallography data were obtained on a Nonius Kappa CCD with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 123(2) K using phi and/or omega scans. The absorptions have been corrected by semi-empirical approach using the SORTAV software [28, 29]. The structures were solved by direct methods and refined by full matrix least squares using SHELX-97 software [30]. The program X-Seed [31] was used as an interface to the SHELX programs and to prepare the figures. In **C1**, all hydrogens were placed in idealized positions, except for the hydrogens on nitrogens, which were located on the Fourier difference map and refined with restrained N–H distances. The isotropic thermal parameters for N–H were fixed at 1.2 times that of the respective nitrogen. The hydrogen atoms associated with the water molecule of crystallization in **C1** could not be located on the Fourier difference map. All hydrogens including those on N2, N3, and N5 in **C2′** were placed in idealized positions. The hydrogens on the remaining nitrogens were located on the Fourier difference map and refined with restrained N–H distances. The isotropic thermal parameters for N–H hydrogens were fixed at 1.2 times that of the respective nitrogen. The cyclen ring was found disordered over two positions and was refined anisotropically using part command. In the figures, the ellipsoids have been drawn at the 50% probability level and hydrogen bonds are represented by dashed lines. Where applicable, # indicates symmetry-generated atoms. Crystal and refinement data can be found in table 1.

Table 1. Crystal data and other parameters.

	C1	**C2′**
Crystal data		
Chemical formula	$C_{23}H_{31}N_5O_{12}Cl_2Cu$	$C_{27}H_{37}N_7O_{11}Cl_2Cd$
M (g M^{-1})	703.97	818.94
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2 (1)/*c*
a (Å)	26.7623(3)	11.6355(2)
b (Å)	13.6980(2)	18.9932(2)
c (Å)	18.5236(3)	16.3893(2)
α (°)	90	90
β (°)	122.7830(10)	110.2380(10)
γ (°)	90	90
Volume (Å^3)	5709.01(14)	3398.35(8)
Z	8	4
D_{Calcd} (Mg m^{-3})	1.638	1.601
θ Range (°)	1.74–25.05	1.70–25.05
Data collection		
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD
Data collection method	Phi and omega scans	Phi and omega scans
Absorption corrections	Multi-scan (*SORTAV*^{21})	Multi-scan (*SORTAV*^{21})
Reflections collected	25,298	29,467
Unique reflections (R_{int})	5041 (0.0418)	6003 (0.0368)
Goodness-of-fit on F^2	1.056	0.992
$F(0\,0\,0)$	2904	1672
R_{int}	0.0418	0.0368
$R_1{}^{a}$, $wR_2{}^{b}$ [$I > 2\sigma(I)$]	0.0582, 0.1502	0.0328, 0.0889
Largest diff. peak and hole (e Å^{-3})	1.214, −0.883	0.594, −0.672

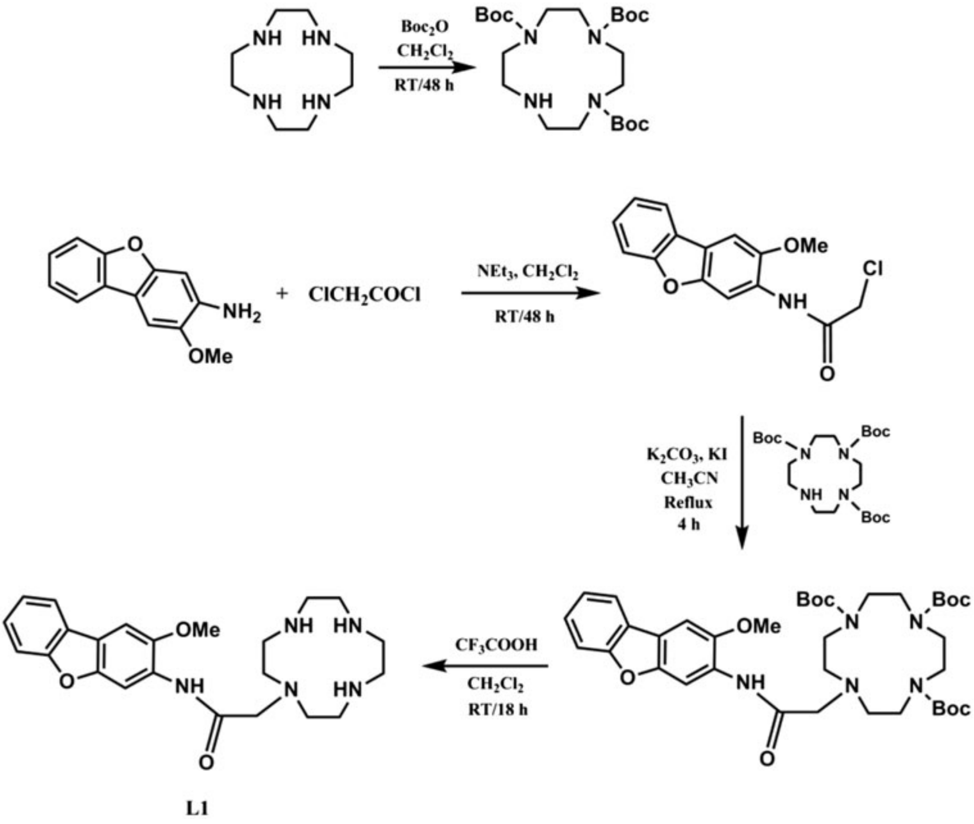
For C1: $^{a}R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^{b}wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.
For C2: $^{a}R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^{b}wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Synthesis and characterization*

The synthesis of the mono-dibenzofuran-substituted cylen ligand, **L1**, was achieved as shown in scheme 1 [27]. It involved condensation of the acetyl chloride derivative of the dibenzofuran with triBoc-protected cyclen in the presence of anhydrous potassium carbonate in acetonitrile followed by deprotection with trifluoroacetic acid [27]. All compounds were characterized by a combination of NMR and IR spectroscopy, and mass spectrometry. The IR spectrum of **L1** showed bands at 3344 cm^{-1} (NH stretch), 2800–2900 cm^{-1} (C–H stretch), 1682 cm^{-1} (C=O stretch), and 1600–1400 cm^{-1} (aromatic ring vibrations). The ^{1}H NMR spectrum showed signals with the expected chemical shifts for the aromatic protons of the dibenzofuran ring (7.8–7.23 ppm) and multiplet signals around 2.81–2.62 ppm for the macrocyclic ring. The ^{13}C NMR spectrum showed four macrocyclic methylene signals and signals for the aromatic carbons of the dibenzofuran units. Finally, the electrospray mass spectrum showed a signal at $m/z = 426$ corresponding to $[M + H]^+$ confirming formation of the compound.

The copper(II) complex, **C1**, prepared by adding copper(II) perchlorate to **L1** in acetonitrile, has a UV–vis absorption band at 590 nm ($\varepsilon = 275$ M^{-1} cm^{-1}). This is in the typical



Scheme 1. Synthesis of **L1** [27].

wavelength range for square pyramidal copper(II) complexes [32–34]. The infrared spectrum of the complex showed a broad N–H stretching band at 3534 cm^{-1} and the characteristic band for C=O at 1643 cm^{-1}. Additionally, bands between 1400–1600 cm^{-1} indicated the presence of the aromatic dibenzofuran moiety. Similarly, the IR spectrum of the cadmium(II) complex, **C2**, prepared by adding cadmium(II) perchlorate to the ligand in acetonitrile, showed a very strong band at 3307 cm^{-1} and a band at 1633 cm^{-1} indicative of the presence of **L1**. Elemental analysis of the Cu(II) and as-isolated Cd(II) complex were consistent with a composition corresponding to [Cu(**L1**)](ClO_4)$_2$·H_2O and [Cd(**L1**)](ClO_4)$_2$·H_2O, respectively.

3.2. *Crystal structures*

3.2.1. [Cu(L1)](ClO_4)$_2$·H_2O (C1). The crystal structure of **C1** shows that the asymmetric unit (ASU) contains a five-coordinate [Cu**L1**]$^{2+}$ cation, two non-coordinating perchlorate anions which balance the charge on the cation, and a disordered oxygen from a water molecule of crystallization. The structure of the cationic unit of **C1** is shown in figure 1, whereas table 2 summarizes key bond lengths and angles for the Cu(II) coordination sphere. Additionally, table 3 presents the parameters for the hydrogen-bonding interactions present in the crystal lattice. The five-coordinate copper(II) center is surrounded by four amine nitrogens from the macrocycle and O(1) from the amide linking the macrocycle to the dibenzofuran moiety. The average Cu–N bond length (ca. 2.025 Å) is within the usual range observed for five-coordinate copper(II)–cyclen complexes [35–37]. A similar trend was previously seen in the case of the analogous bis-dibenzofuran copper(II) complex, which also showed similar coordination [24]. Distortion of the copper(II) geometry is highlighted by the significant variation in Cu–N distances (>0.06 Å) and the various N–Cu–N angles. The amide oxygen, O(1), from the pendant arm occupies the axial position, with Cu–O(1)

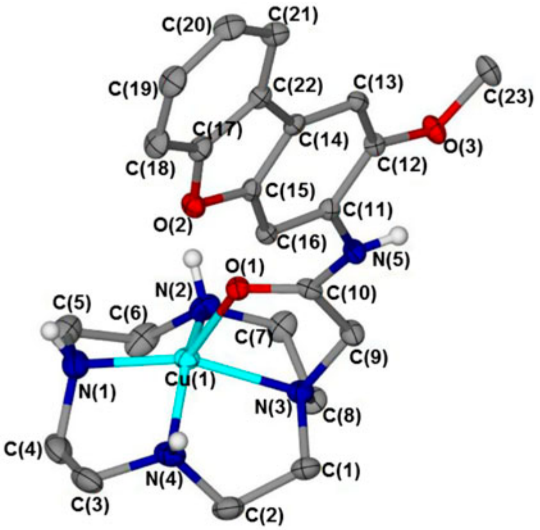


Figure 1. Thermal ellipsoid representation of the complex cation in **C1** (ellipsoids drawn at 50% probability; selected hydrogens, non-coordinating solvent molecule, and the counter anions have been omitted for clarity).

Table 2. Selected bond distances (Å) and angles (°) for **C1**.

Cu(1)–N(4)	1.990(4)	N(1)–Cu(1)–N(2)	86.28(19)
Cu(1)–N(1)	2.001(4)	N(4)–Cu(1)–N(3)	87.30(16)
Cu(1)–N(2)	2.043(4)	N(1)–Cu(1)–N(3)	152.48(16)
Cu(1)–N(3)	2.057(4)	N(2)–Cu(1)–N(3)	84.63(16)
Cu(1)–O(1)	2.168(3)	N(4)–Cu(1)–O(1)	97.66(15)
		N(1)–Cu(1)–O(1)	127.67(14)
N(4)–Cu(1)–N(1)	87.34(19)	N(2)–Cu(1)–O(1)	110.00(15)
N(4)–Cu(1)–N(2)	149.21(12)	N(3)–Cu(1)–O(1)	79.82(12)

Table 3. Hydrogen-bonding interactions in **C1** [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(4)–H(4N)···O(9)#1	0.87(2)	2.24(3)	3.069(8)	159(5)
N(1)–H(1N)···O(6)#2	0.88(2)	2.16(2)	3.038(6)	170(5)
N(2)–H(2N)···O(10)#3	0.87(2)	2.07(2)	2.925(6)	170(5)
N(5)–H(5N)···O(3)	0.86(2)	2.21(5)	2.595(5)	107(4)
N(5)–H(5N)···O(4)	0.86(2)	2.39(3)	3.164(5)	150(5)

distance [2.168(3) Å] longer than the Cu–N distances. Further, the copper(II) center sits above the basal plane defined by the four macrocyclic nitrogens by 0.507(0.002) Å, as expected for such square pyramidal copper(II) complexes. Quantification of the degree of distortion of the copper(II) coordination sphere according to the method developed by Addison *et al.* [38] yielded a τ value of 0.055, calculated from the bond angles N(1)–Cu (1)–N(3) (152.48(16)) and N(4)–Cu(1)–N(2) (149.21(12)). This value is much closer to that expected for an ideal square pyramidal geometry ($\tau = 0$), rather than a trigonal bipyramidal geometry ($\tau = 1.0$).

Within the structure, intermolecular hydrogen-bonding interactions are observed between a perchlorate and the amide nitrogen N(5). There is also a strong intramolecular hydrogen bond between N(5) and the ether oxygen O(3) from the dibenzofuran ring, as shown in figure 2, with a N···O distance of 2.595(5) Å (table 3). The perchlorates are simultaneously involved in H bonding to one of the nitrogens from the macrocycle. Figure 2(a) and (b) shows the arrangement of cationic [Cu(**L1**)]$^{2+}$ units and perchlorate counter anions within the crystal lattice of **C1**, linked to each other via hydrogen-bonding interactions.

3.2.2. [Cd(L1)(CH3CN)2](ClO4)2 (C2′). The crystal structure of **C2′**, a derivative of **C2** obtained by recrystallization of **C2** from acetonitrile, consists of discrete [Cd(**L1**)(CH$_3$CN)$_2$]$^{2+}$ cationic units and two non-coordinated perchlorates. A thermal ellipsoid representation of the complex cation is shown in figure 3, while key bond lengths and angles for the Cd(II) coordination sphere are listed in table 4. Additionally, table 5 summarizes the hydrogen-bonding interactions present in the crystal lattice of **C2′**. The Cd(II) center is seven coordinate, with the coordination sphere occupied by four nitrogen amines from the macrocycle, two nitrogens from weakly coordinating acetonitrile molecules, and O1 from the amide group, which links the dibenzofuran moiety to the macrocycle in **L1**. The Cd(II) center can be best described to reside in a distorted monocapped trigonal prismatic geometry (figure 4), compared to the more common pentagonal bipyramidal or monocapped octahedral geometry observed for seven-coordinate metal complexes [39–48]. As proposed by

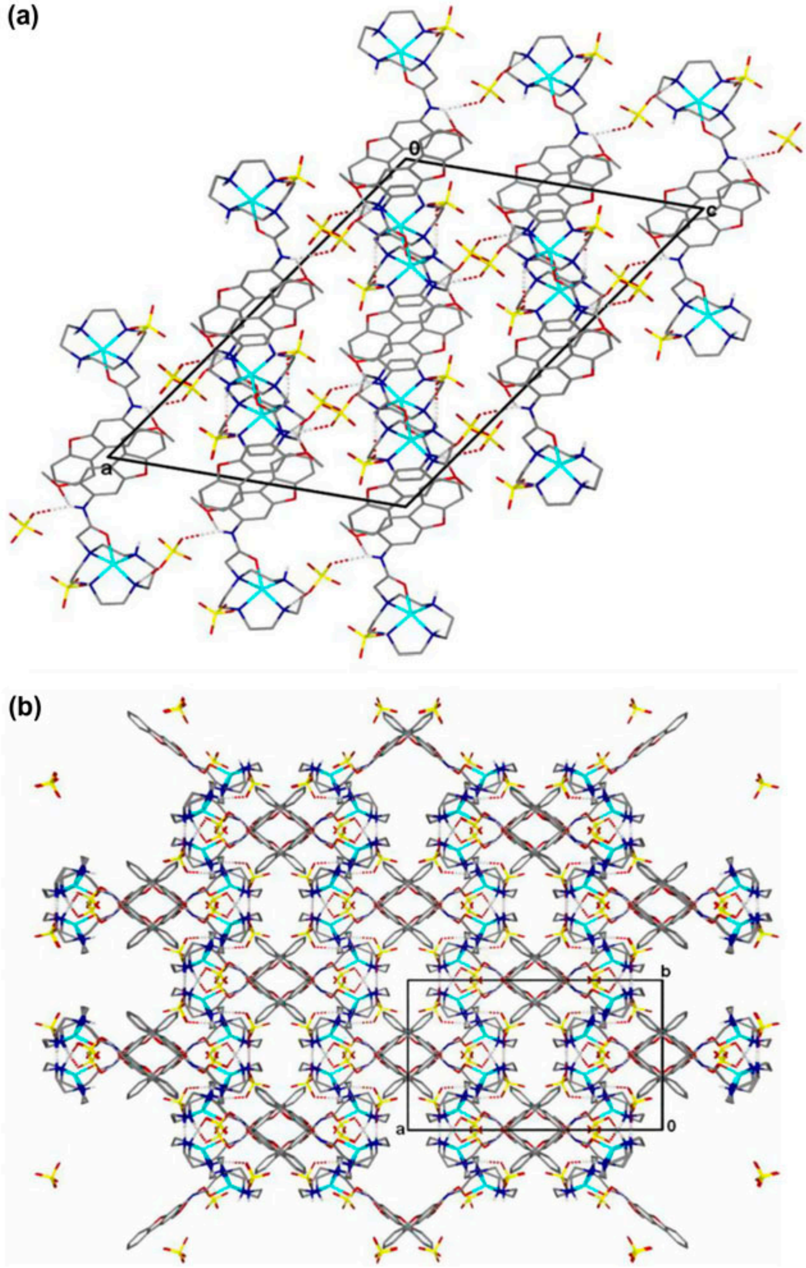


Figure 2. Stick representation of (a) the unit cell contents in **C1** viewed down the *b* axis direction, showing H bonding as dashed bonds; and (b) crystal packing in **C1**, viewed down the *c* axis (non-coordinating oxygens associated with the co-crystallized water molecule and selected H atoms have been omitted for clarity).

Amoroso *et al.* [49], the degree to which a complex resembles either a monocapped octahedron or capped trigonal prism can be ascertained from the angle between the atoms N(10)–Cd–N(1) and N(10)–Cd–N(2). In an ideal monocapped octahedron, one of these

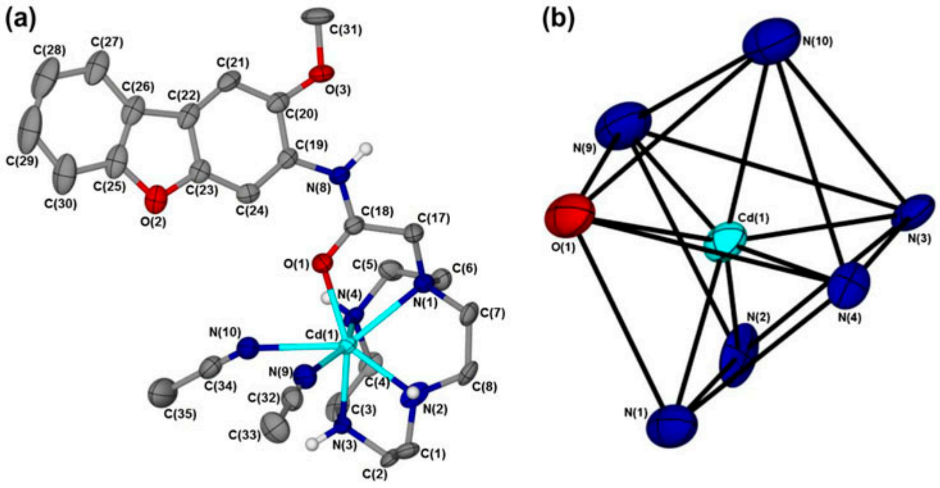


Figure 3. Left: Molecular structure of **C2′** with atoms shown as thermal ellipsoids (drawn at 50% probability; aryl/alkyl hydrogens and the perchlorate counterions are omitted for clarity). Right: Molecular geometry of the seven-coordinate Cd(II) center of **C2′** residing in a monocapped trigonal prismatic geometry.

Table 4. Selected bond distances (Å) and angles (°) for **C2′**.

Cd(1)–N(2)	2.242(9)	O(1)–Cd(1)–N(3)	156.75(19)
Cd(1)–O(1)	2.2665(19)	N(2)–Cd(1)–N(4)	116.6(3)
Cd(1)–N(3)	2.388(7)	O(1)–Cd(1)–N(4)	93.5(2)
Cd(1)–N(4)	2.460(10)	N(3)–Cd(1)–N(4)	73.9(3)
Cd(1)–N(1)	2.485(3)	N(2)–Cd(1)–N(1)	78.9(3)
Cd(1)–N(9)	2.439(3)	O(1)–Cd(1)–N(1)	71.48(8)
Cd(1)–N(10)	2.591(3)	N(3)–Cd(1)–N(1)	110.00(15)
N(2)–Cd(1)–O(1)	126.2(2)	N(2)–Cd(1)–N(3)	77.0(3)
N(4)–Cd(1)–N(1)	69.3(2)	N(2)–Cd(1)–N(10)	144.3(3)
N(2)–Cd(1)–N(9)	81.7(3)	O(1)–Cd(1)–N(10)	81.40(8)
O(1)–Cd(1)–N(9)	83.98(9)	N(3)–Cd(1)–N(10)	77.02(18)
N(9)–Cd(1)–N(4)	157.9(2)	N(9)–Cd(1)–N(10)	79.36(9)
N(9)–Cd(1)–N(5)	79.64(16)	N(4)–Cd(1)–N(10)	78.6(2)
N(3)–Cd(1)–N(9)	100.3(2)	N(5)–Cd(1)–N(10)	154.12(17)
N(9)–Cd(1)–N(1)	129.53(10)	N(1)–Cd(1)–N(10)	135.82(9)

Table 5. Hydrogen-bonding interactions in **C2′** [Å and °].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(6)–H(6N)···O(6)#2	0.88(2)	2.19(2)	3.059(6)	170(7)
N(7)–H(7N)···O(10)#3	0.88(2)	2.59(8)	3.329(8)	142(11)
N(4)–H(4N)···O(10)#3	0.88(2)	2.39(6)	3.216(10)	156(13)
N(4)–H(4N)···O(11)#3	0.88(2)	2.67(13)	3.204(11)	120(11)
N(8)–H(8N)···O(3)	0.89(4)	2.17(4)	2.582(3)	107(3)
N(8)–H(8N)···O(7)#1	0.89(4)	2.30(4)	3.148(3)	161(4)
N(8)–H(8N)···O(5)#1	0.89(4)	2.64(4)	3.092(3)	112(3)
N(5)–H(5N)···O(8)	0.93	2.26	3.005(8)	136.6
N(5)–H(5N)···O(10)	0.93	2.53	3.411(8)	159.0
N(3)–H(3N)···O(6)#2	0.93	2.12	3.047(7)	172.8
N(2)–H(2N)···O(8)	0.93	2.68	3.535(9)	152.6

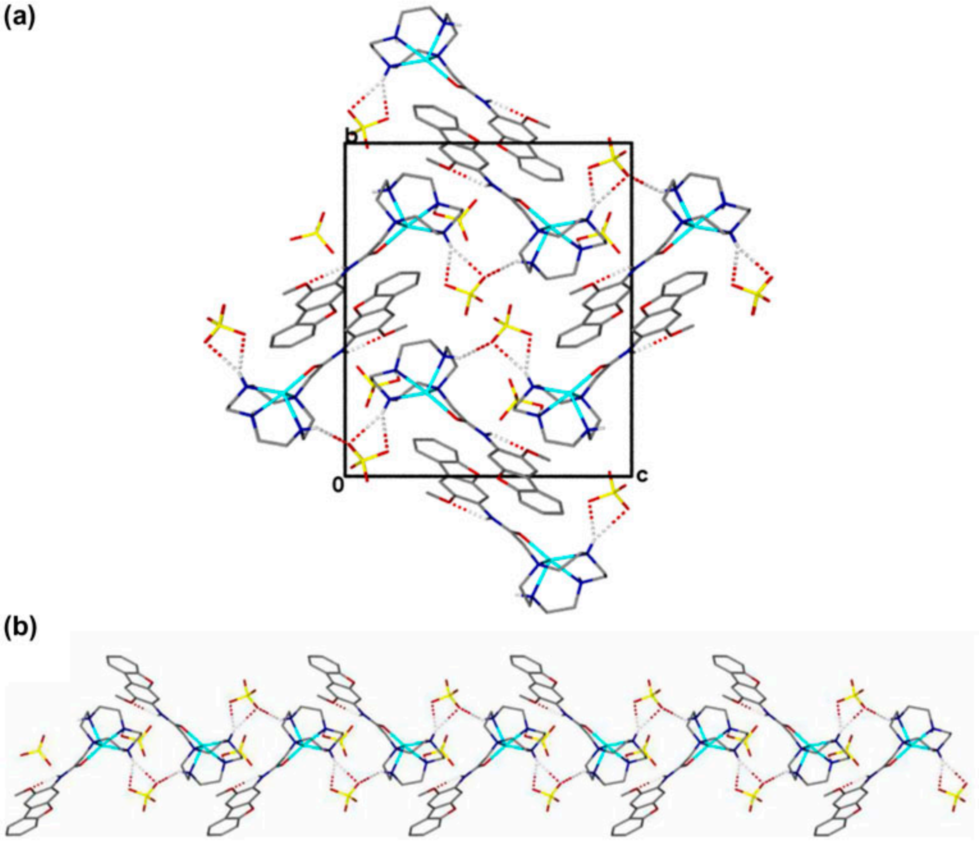


Figure 4. Stick diagram showing (a) H-bonding interactions (shown as dashed bonds) and the unit cell contents in **C2′** viewed along the *a* axis; and (b) a segment of a “zig-zag” arrangement of **C2′** units, formed due to intermolecular H bonding between the complex cation and perchlorate counter anions (H bonding shown as dashed bonds; phenyl/alkyl hydrogens, and metal ion coordinating CH_3CN molecules omitted for clarity).

angles should be 180°, while the other should be around 125°, whereas for an ideal capped trigonal prismatic geometry, these angles should be equal. In our case, the respective angles are 135.8(9)° for N(10)–Cd–N(1) and 144.3(3)° for N(10)–Cd–N(2). The distortion of the Cd(II) coordination sphere geometry from an ideal monocapped octahedron towards the monocapped trigonal prismatic geometry can be estimated from the ratio of the difference in these two apical angles; the maximum possible difference is 55° for an ideal monocapped octahedron. In our case, the calculated value of 15% (8.48 × 100/55) can be interpreted to indicate that the geometry around the Cd(II) center is 85% monocapped trigonal prismatic and 15% monocapped octahedral in character [49].

It appears that the Cd–N(2), Cd–O(1), and Cd–(N(3) bond lengths (2.242(9), 2.2665(19), and 2.388(7) Å) are unusually small compared to the average bond length observed for seven-coordinate cadmium(II) complexes with nitrogen donor ligands (2.41–2.44 Å) [49], also deviating from the typical lengths observed in cyclen complexes of this metal ion [50, 51]. This could be due to geometrical restraints imposed by coordination of the amide O1 to Cd(II).

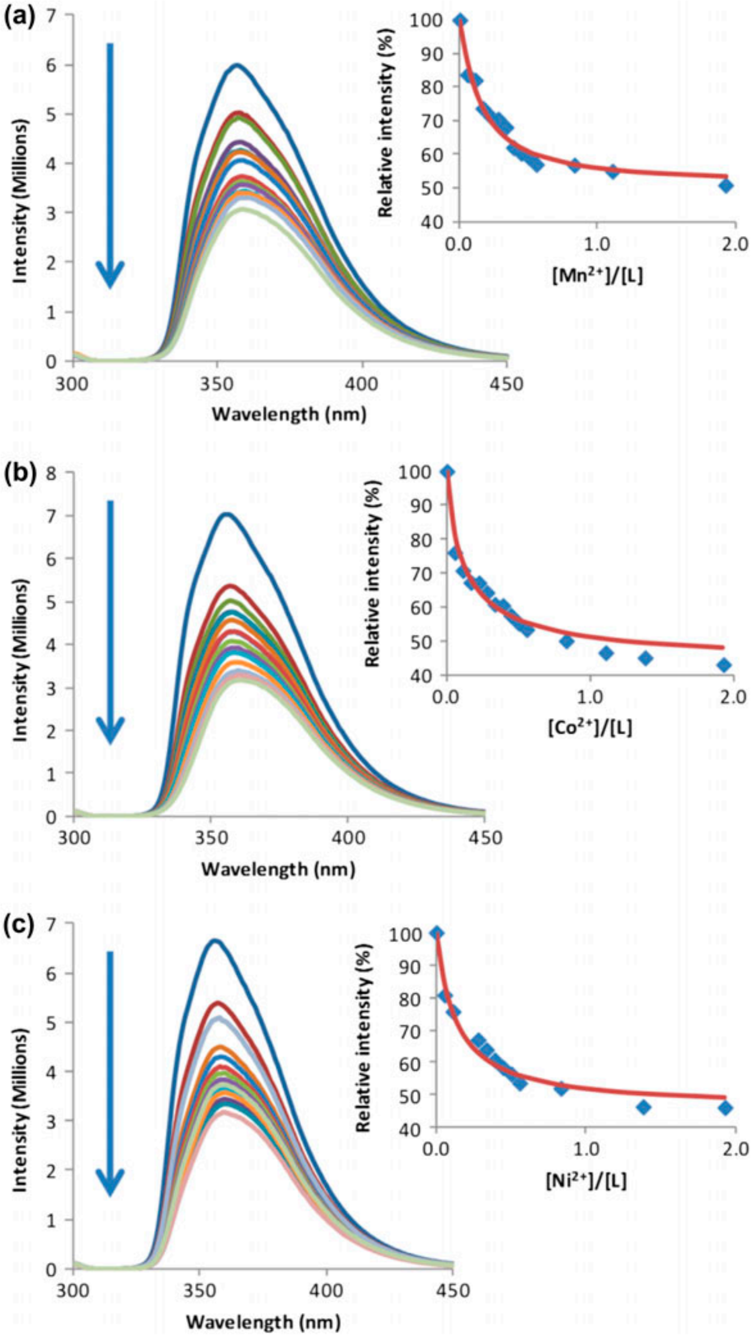


Figure 5. Quenching of the emission of **L1** (33.3 μM) on addition of (a) Mn^{2+}, (b) Co^{2+}, (c) Ni^{2+}, (d) Cd^{2+}, (e) Zn^{2+}, and (f) Cu^{2+} in CH_3CN.

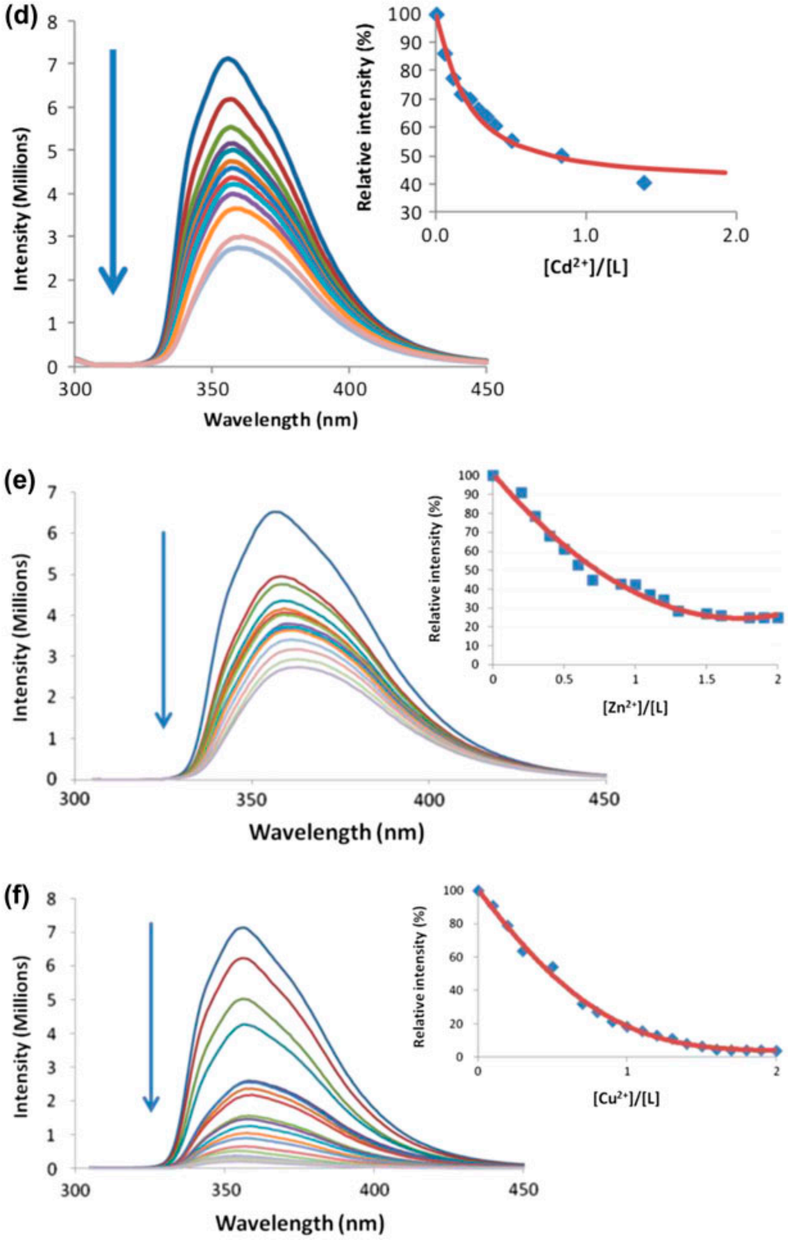


Figure 5. (*Continued*).

Within the structure of **C2′**, extended intermolecular hydrogen-bonding interactions are observed between a perchlorate and the macrocyclic nitrogens [figure 4(a) and (b)]. The hydrogen-bonding distances for these interactions are 0.88(2) Å (N(4)–H(4N)···O(10)#3) and 0.88(2) Å (N(4)–H(4N)···O(11)#3). As in **C1**, a strong intramolecular hydrogen bond exists between the amide N–H and the ether oxygen, N(8)–H(8N)···O(3) = 2.582(3) Å.

3.3. *Fluorescence measurements*

Initial fluorescence emission studies conducted for free **L1** revealed it to have an emission band at 360 nm when excited at 300 nm, which is similar to that observed for the bis-dibenzofuran-substituted cyclen compound reported earlier [27]. The emission spectrum shows a slight shoulder around 350 nm, indicating that emission could be taking place from two excited states. Various metal ions were added, systematically increasing their concentration, to evaluate the ability of these metal ions to affect the fluorescent emission of the free ligand. The metal ions chosen for this study included Cd^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}, whereas the effect of Zn^{2+} and Cu^{2+} ions has been studied before [27]. Herein, we have repeated the experiments with Zn^{2+} and Cu^{2+} to estimate the conditional stability constants. The addition of the metal ions resulted in quenching of the fluorescence, with no further decrease observed when the $[M^{2+}]$: **L1** ratio exceeded 1 : 1. The titration curves are shown in figure 5. In contrast to the case of the bis-dibenzofuran-substituted cyclen ligand, where addition of copper ions totally eliminated the fluorescent emission [27], the emission intensity decreased but not completely to zero. In our earlier report [27], a similar observation was made for the addition of Zn^{2+} to **L1**. Binding of the oxygen from the amide group is postulated to be responsible for totally or partially quenching the fluorescence. Ryan and Weber [52] described how similar systems are characterized by the quenching of fluorescence to a limiting intensity value $I_{ML,}$ where all the metal has reacted with the ligand and there is no further fluorescence intensity decrease upon addition of more metal ions. In the case of Cu^{2+} addition to the mono-dibenzofuran ligand, this value is less than for other metal ions [27]. The conditional stability constant (K) may be different for each of the metal complexes and could be (partly) responsible for the observed trend. To evaluate this, the relative intensity (y) was plotted against metal ion concentration (x) and the 1 : 1 M^{2+}–**L1**-binding stoichiometry was confirmed for each metal ion. Analysis of the data using the following equation gave the conditional stability constant, K [53]:

$$y = \frac{a + bKx^n}{1 + Kx^n}$$

where a represents the intensity of the ligand in the absence of metal, b is the intensity when excess metal has been added and corresponds to I_{ML}, and n indicates the $[M^{2+}]$: ligand stoichiometry in the complex. Table 6 summarizes the values obtained for each metal ion. The conditional stability constants are of the order of 10^6 M^{-1} and in accord with the

Table 6. Conditional stability constants (K) for the M^{2+} complexes and their respective, experimentally obtained, in-solution stoichiometry.

Metal ion	K (μM^{-1})	n
Mn(II)	0.08 ± 0.02	1.15 ± 0.11
Co(II)	0.17 ± 0.05	0.88 ± 0.09
Ni(II)	0.12 ± 0.04	1.03 ± 0.10
Cu(II)[18]	1.16 ± 0.28[a]	1
Zn(II)[18]	0.11 ± 0.03[a]	1
Cd(II)	0.05 ± 0.02	1.22 ± 0.16

[a] The 1 : 1 conditional stability constants (K) were obtained using the equation described by Ryan and Weber [27, 52].

Irving–Williams series, which predicts that the Cu(II) complex will have the highest stability constant amongst the studied first-row divalent transition metal ions [54, 55].

4. Conclusion

The metal complexes (Cu^{2+}, Cd^{2+}) of a mono-dibenzofuran-substituted cyclen ligand have been prepared and their structures determined by X-ray crystallography. The crystal structure of the copper(II) complex revealed that Cu(II) resides in a five-coordinate distorted square-pyramidal geometry, as is common for the copper(II) complexes of cyclen derivatives. The Cd(II) center, on the other hand, is seven-coordinate with two acetonitrile ligands also occupying the metal coordination sphere, and exhibits an uncommon, distorted monocapped trigonal prismatic geometry. In both cases, coordination to the oxygen of the amide group of the dibenzofuran pendant arm is observed. Furthermore, addition of various transition metal ions (Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) was universally found to quench the emission of the dibenzofuran ligand. Fluorescence titrations established a 1 : 1 M^{2+}–**L1**-binding stoichiometry for each of the divalent metal ions. A determination of the conditional stability constants revealed that the binding affinity is highest for Cu^{2+} by 10–20-fold, in accord with the Irving–Williams series [54].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC # 876318 for **C2** and 876319 for **C1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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