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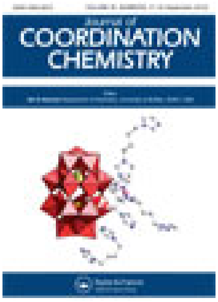

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Syntheses and structures of Mn(II), Co(II), and Zn(II) complexes of 1,3-diterpyridyl-substituted p-tert-butylcalix[4]arene

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Syntheses and structures of Mn(II), Co(II), and Zn(II) complexes of 1,3-diterpyridyl-substituted *p-tert*-butylcalix[4]arene

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The calix[4]arene-based podand which incorporates two terpyridine functions in 1,3-alternate positions with flexible propylene spacers at lower rim has been prepared and subjected to complexation studies with some transition metal ions. Single-crystal structures of Mn(II), Co(II), and Zn(II) complexes were determined by X-ray diffraction. These metal complexes are formed with a 2 : 1 ratio of metal and ligand. Coordination of each metal is five-coordinate distorted trigonal-bipyramidal geometry by three nitrogen atoms from a terpyridyl unit and two chloride atoms.

Keywords: Calixarene; Terpyridine; Metallic complex; Transition metal; Crystal structure

1. Introduction

Calixarenes, macrocyclic compounds available in a variety of ring sizes, are widely used synthetic macrocycles possessing extensive host–guest chemistry [1]. Interest has focused on the use of calixarenes as inclusion hosts, selective receptors, molecular sensors, and building blocks for supramolecular chemistry [2, 3]. Coordination chemistry of calixarenes has shown these compounds as selective binders, carriers, and also as building blocks for complexes [4–6]. The relative rigid organic backbone of calix[4]arenes provides a platform for assembly of several metals in relatively close proximity. The vast majority of these metallocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the parent ligands [7–9]. 2,2′ : 6′,2″-Terpyridine represents a highly versatile tridentate ligand, employed widely in formation of transition metal complexes owing to their applications in electrochemistry, supramolecular assembly, emitters for electroluminescence devices, and molecular probes [10, 11]. Combination of terpyridine and calixarene properties into a unique entity could give interesting systems with peculiar coordination properties. Several works have demonstrated the introduction of terpyridine function onto the lower or upper rim of calixarenes and used them as functionalized ligands to

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coordinate transition metal ions. Parrot-Lopez firstly prepared tetrakis-terpyridinyl-calix[4]arene by coupling tetrasuccinimidyl activated ester of *p*-*tert*-butylcalix[4]arene with 4′-(2-aminoethoxy)-2,2′ : 6,2″-terpyridine and used it as a rigid scaffold and pre-organizer of supramolecular assemblies by complexation of Ni(II), Cu(II), and Co(II) [12]. Wu and Tong reported the synthesis of 1,3-terpyridyl-substituted calix[4]arene and the respective complexation of Fe(II), Zn(II), or Ni(II) by monitoring UV absorption spectra [13]. Volkmer introduced terpyridine onto the upper rim of calix[n]arene ($n = 4$, 5) by Suzuki cross-coupling of *p*-bromocalix[*n*]arenes with functionalized 4-glycolatoboronphenyl2,2′ : 6′,2″-terpyridine [14]. They also prepared tetra-(4 -(2,2′ : 6′,2″-terpyridyl)-phenyl)-cavitand by Suzuki-coupling of tetraiodocavitand and obtained a discrete cavitand-based hexameric cage complex by metal-directed self-assembly [15]. There are also reports on using functionalized calixarenes and terpyridines as mixed ligands to construct metal complexes and assemble multi-component nanocapsule and layer structures [16]. However, preparation and crystal structures of transition metal complexes of calixarene terpyridines have not yet been investigated in detail. As part of our ongoing investigation of coordination environments afforded by calixarene-based ligands [17], herein we report the investigation of 1,3-alternate terpyridine ligands with calix[4]arene as a platform for construction of transition metal complexes.

2. Experimental

2.1. *Material and apparatus*

2-Pyridinecarboxylic acid, 1-bromo-3-chloropropane, 1-bromo-4-chlorobutane, and other reagents are commercial reagents and used as received. *p*-*tert*-Butylcalix[4]arene [18] and 2,6-di(2-pyridyl)-4-pyridinone [19] were prepared according to the published method. Solvents were purified by standard techniques. All reactions were monitored by thin layer chromatography. Melting points were taken on a hot-plate microscope apparatus. IR spectra were obtained on a Bruker Tensor 27 spectrometer (KBr disc). NMR spectra were recorded with a Bruker AV-600 spectrometer with DMSO-d_6 as solvent and TMS as internal standard (600 and 150 MHz for ^{1}H and ^{13}C NMR spectra, respectively). X-ray data were collected on a Bruker Smart APEX-2 diffractometer.

2.2. *Synthesis of 4′-(ω-chloropropoxy)-2,2′ : 6′,2″-terpyridine (1a)*

A mixture of 2,6-di(2-pyridyl)-4-pyridinone (40.0 mmol, 9.92 g), potassium carbonate (120.0 mol, 16.56 g), and acetone (100 mL) was heated to reflux for one hour. Then 1-bromo-3-chloropropane (48.0 mol, 7.56 g) was added and the mixture was stirred at reflux for 5 days. After cooling to room temperature the solution was filtered and concentrated to 30 mL. Then water (100 mL) was added and the resulting oily residue was extracted with chloroform (100 mL). After evaporating the solvent, the crude product was recrystallized with ethanol to give pure **1a**: white solid, 76%, m.p. 95–96°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.69 (d, $J = 4.8$ Hz, 2H, ArH), 8.61 (d, $J = 8.4$ Hz, 2H, ArH), 8.03 (s, 2H, ArH), 7.84 (t, $J = 7.8$ Hz, 2H, ArH), 7.34–7.32 (m, 2H, ArH), 4.39 (t, $J = 6.0$ Hz, 2H, CH_2), 3.78 (t, $J = 6.0$ Hz, 2H, CH_2), 3.33–2.29 (m, 2H, CH_2);

^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.9, 157.1, 156.0, 149.0, 136.8, 123.9, 121.3, 107.3, 64.4, 41.2, 32.0; IR(KBr) ν: 3058, 2957, 1581, 1561, 1470, 1443, 1409, 1359, 1277, 1252, 1198, 1123, 1094, 1043, 989, 964, 872, 794 cm^{-1}; MS(m/z): 326.72 $[M+1]^+$100%, 328.75 $[M+3]^+$ 53%.

2.3. *Synthesis of p-tert-butylcalix[4]arene-1,3-di(4′-propoxy-2,2′ : 6′,2″-terpyridine) (2a)*

A mixture of *p-tert*-butylcalix[4]arene (3.0 mmol, 1.95 g), potassium carbonate (24.0 mmol, 3.40 g), and potassium iodide (7.0 mmol, 1.20 g) in dry acetone (100 mL) was stirred at room temperature for 2 h. Then **1a** (7.0 mmol, 2.28 g) was added and the mixture was refluxed for 6 days. The solution was filtered and solvent was evaporated. Then water (100 mL) was added and pH was adjusted to neutral by using dilute hydrochloric acid. The resulting precipitate was collected by filtration and recrystallized with ethanol to give pure **2a**: white solid, 80%, m.p. 202–204°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.62 (d, $J=4.2$ Hz, 4H, ArH), 8.51 (d, $J=7.8$ Hz, 4H, ArH), 8.06 (s, 4H, ArH), 7.77–7.75 (m, 6H, ArH), 7.25 (s, 1H, ArH), 7.05 (s, 1H, ArH), 6.95 (s, 4H, ArH), 6.83 (s, 4H, ArH), 4.74 (t, $J=6.0$ Hz, 4H, CH_2), 4.19 (d, $J=13.2$ Hz, 4H, CH_2), 4.16 (t, $J=6.0$ Hz, 4H, CH_2), 3.24 (d, $J=13.2$ Hz, 4H, CH_2), 2.57–2.53 (m, 4H, CH_2), 1.23 (s, 18H, CH_3), 0.99 (s, 18H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 167.0, 156.9, 156.1, 150.6, 149.5, 148.9, 146.9, 141.1, 136.6, 132.8, 127.4, 125.5, 125.0, 123.6, 121.3, 107.6, 72.5, 64.6, 34.0, 33.7, 31.8, 31.7, 31.4, 31.0, 29.7; IR(KBr) ν: 3373, 3050, 2959, 2870, 1752, 1583, 1564, 1482, 1445, 1408, 1361, 1301, 1202, 1124, 1094, 1052, 1001, 926, 872, 818, 793 cm^{-1}.

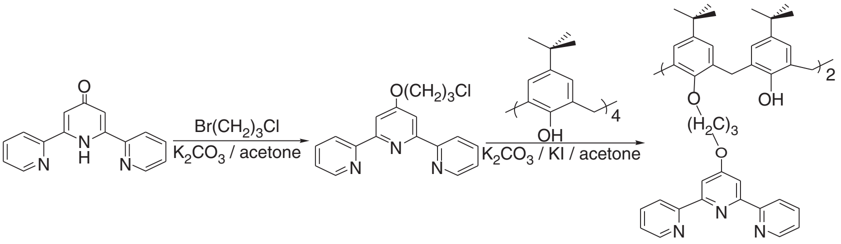
2.4. *Synthesis of transition metal complexes of p-tert-butylcalixarene-1, 3-bisterpyridines*

Transition metal chloride $MnCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2 \cdot 6H_2O$ (0.6 mmol) in methanol (15 mL) was added very slowly to **2a** (0.3 mmol) in chloroform (10 mL). The resulting solution was kept at room temperature for 1 day. The resulting solid was collected, washed with cold methanol, and dried in air to give: **2a-Mn**: light yellow solid, m.p. > 250°C; IR (KBr) ν: 3063, 2955, 2867, 2673, 1602, 1561, 1480, 1435, 1386, 1363, 1297, 1255, 1204, 1163, 1093, 1054, 1031, 983, 940, 871, 796 cm^{-1}; **2a-Co**: green solid, m.p. > 250°C; IR (KBr) ν: 3061, 2957, 2867, 1670, 1606, 1565, 1479, 1437, 1365, 1298, 1222, 1162, 1123, 1094, 1034, 872, 796 cm^{-1}; **2a-Zn**: white solid, m.p. >250°C; IR (KBr) ν: 3065, 2957, 2967, 1671, 1604, 1571, 1480, 1437, 1365, 1298, 1256, 1205, 1164, 1124, 1091, 1054, 872, 796 cm^{-1}.

3. Results and discussion

3.1. *Syntheses and characterizations*

Calix[4]arene-1,3-bis(terpyridine) was prepared in two steps by reactions depicted in scheme 1. First, 2,6-di(2-pyridyl)-4-pyridinone was *O*-alkylated with 1-bromo-3-chloropropane in K_2CO_3/acetone to give 4′-(ω-chloropropoxy)-2,2′ : 6′,2″-terpyridine (**1a**)



Scheme 1. Synthesis of calix[4]arene bisterpyridine ligand.

according to the adjusted literature method [20, 21]. Second, 1,3-dialkylation of *p-tert*-butylcalix[4]arene with **1a** in the system of $K_2CO_3/KI/CH_3CN$ for 6 days gave the expected calix[4]arene-1,3-bisterpyridine ligand **2a** in good yields (scheme 1). Complex **2a** was characterized by IR and ^{1}H, ^{13}C NMR spectra. The ^{1}H NMR spectrum of **2a** displays doublets at 3.24 and 4.19 ppm with geminal coupling constants $J = 13.2$ Hz for the methylene bridge protons of the calix[4]arene ring. This typical AB pattern for the axial and equatorial protons indicates that **2a** exists in symmetrical *cone* conformation. Two singlets at 1.23 and 0.99 ppm for *t*-butyl protons in the ratio of 1 : 1 also suggest two kinds of *t*-butylphenyl groups. The bridging propylene groups display two triplets at 4.16 and 4.74 ppm and overlapping peaks at 2.57–2.53 ppm, which also shows that the two bridging arms are magnetically equivalent.

The molecular structures of **1a** and **2a** were successfully determined by X-ray diffraction methods, figures 1 and 2, respectively. Crystal data and refinement details are listed in table 1. The crystal structures indicate that calix[4]arene-1,3-bis(terpyridine) was successfully synthesized. From figure 2 we see that the calixarene core exists in *cone* conformation. Two H-bonds were formed between the unsubstituted phenolic hydroxyl and oxygen of ether groups. The two propylene bridging terpyridyl groups stretch to the outer positions at the lower rim of the calixarene. The three pyridyl rings in the terpyridine unit deviate from the same plane due to no complexation.

3.2. *Syntheses and structures of metal complexes*

The Mn(II), Co(II), and Zn(II) complexes of calix[4]arene-1,3-bis(terpyridines) were successfully prepared by the reaction of ligands with transition metal chloride in methanol/chloroform solution. The molecular structures of complexes have been established by single-crystal X-ray diffraction of **2a-Mn**, **2a-Co**, and **2a-Zn**, which were formed when a chloroform/methanol solution was allowed to slowly evaporate for a couple of weeks. Perspective views with typical atom-numbering scheme are shown in figures 3–5, respectively. Crystal data and refinement details are given in table 1. Selected bond distances and angles are summarized in table 2. The three crystals have similar structures with calix[4]arene as backbone and two terpyridyl units as two independent tridentate ligands. The calix[4]arene remains in the *cone* conformation. As each terpyridyl coordinated to one metal, the three metal complexes are formed with a 2 : 1 ratio of metal and ligand. Each metal is five-coordinate by three nitrogen atoms from a terpyridine unit and two chloride atoms and the three complexes are very similar

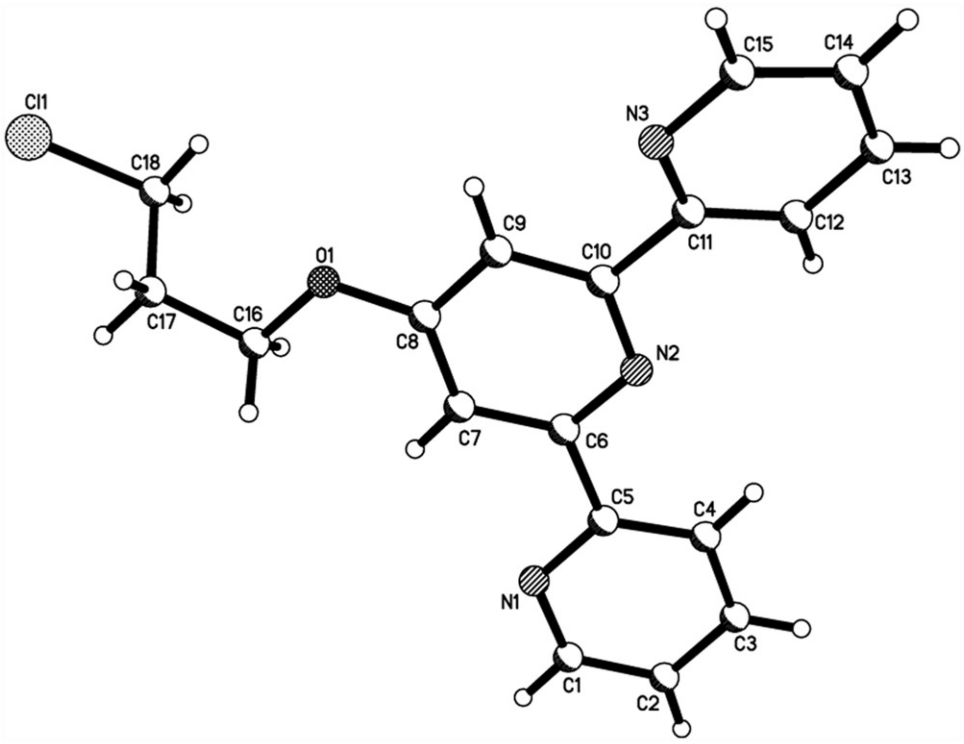


Figure 1. Molecular structure of **1a**.

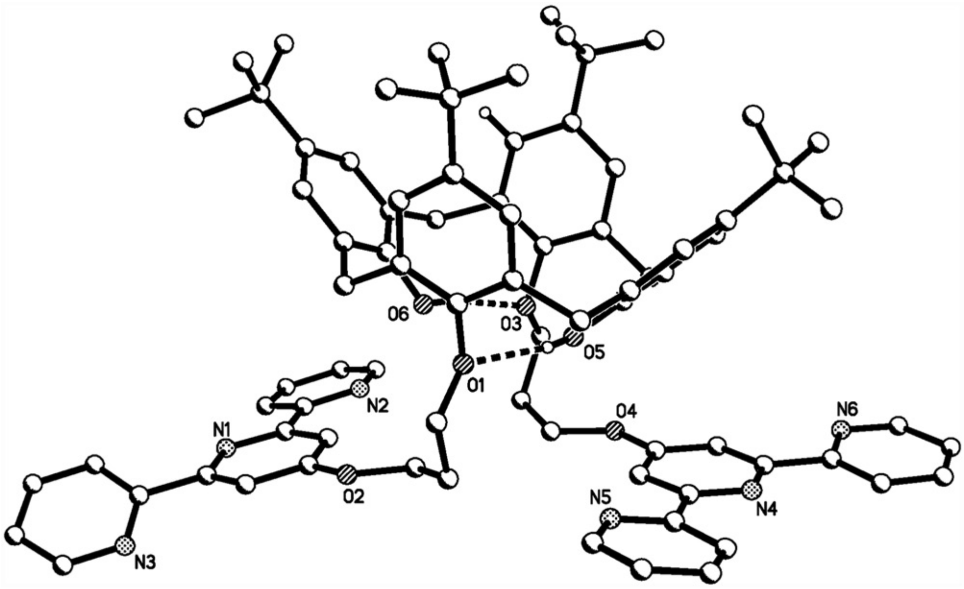


Figure 2. Molecular structure of **2a**.

Table 1. Crystal data of **1a** and **2a**.

Phase	**1a**	**2a**	**2a-Mn**	**2a-Co**	**2a-Zn**
Empirical formula	$C_{18}H_{16}ClN_3O$	$C_{80}H_{86}N_6O_6$	$C_{95}H_{121}Cl_4Mn_2N_{11}O_{11}$	$C_{80}H_{86}Cl_4Co_2N_6O_6$	$C_{80}H_{86}Cl_4N_6O_6Zn_2$
Formula weight	325.79	1227.55	1844.71	1487.21	1500.13
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Color	Colorless	Colorless	Yellow	Green	Colorless
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pc*	*P*-1	*P*21/*c*	*P*21/*c*	*P*21/*c*
Unit cell dimensions (Å, °)					
a	6.076(3)	14.189(3)	13.9315(12)	13.9137(17)	13.8804(11)
b	8.983(5)	16.048(3)	36.863(3)	37.081(5)	37.125(3)
c	15.704(8)	17.526(4)	19.8151(16)	19.524(2)	19.6612(16)
α	90	79.619(3)	90	90	90
β	106.659(17)	72.437(3)	109.1340(10)	109.081(2)	109.1930(10)
γ	90	77.156(3)	90	90	90
Volume ($Å^3$), Z	821.2(7), 2	3682.0(13), 2	9614.0(14), 4	9524(2), 4	9568.5(13), 4
Calculated density ($g\,cm^{-3}$)	1.318	1.107	1.275	1.037	1.041
Absorption coefficient (mm^{-1})	0.240	0.07	0.437	0.505	0657
$F(000)$	340	1312	3896	3112	3136
θ range for data collection (°)	2.27–25.98	1.68–27.95	1.55–27.59	1.55–27.61	1.55–27.83
Reflections collected	6107	31,847	84,530	84,102	86,266
Independent reflection	1627 [R(int) = 0.0432]	17,671 [R(int) = 0.0771]	22,269 [R(int) = 0.0591]	22,111 [R(int) = 0.1216]	22,711 [R(int) = 0.0977]
Data/restraints/parameters	1626/2/208	16,859/0/842	22,131/11/1180	21,916/2/897	22,470/0/897
Goodness-of-fit on F^2	1.082	0.995	1.021	0.839	0.845
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0819$	$R_1 = 0.0897$, $wR_2 = 0.2365$	$R_1 = 0.0796$, $wR_2 = 0.2132$	$R_1 = 0.0619$, $wR_2 = 0.1252$	$R_1 = 0.0522$, $wR_2 = 0.1203$
Largest difference peak and hole ($e\,Å^{-3}$)	0.300 and −0.15	1.491 and −0.910	0.905 and −0.755	0.520 and −0.480	0.825 and −0.600

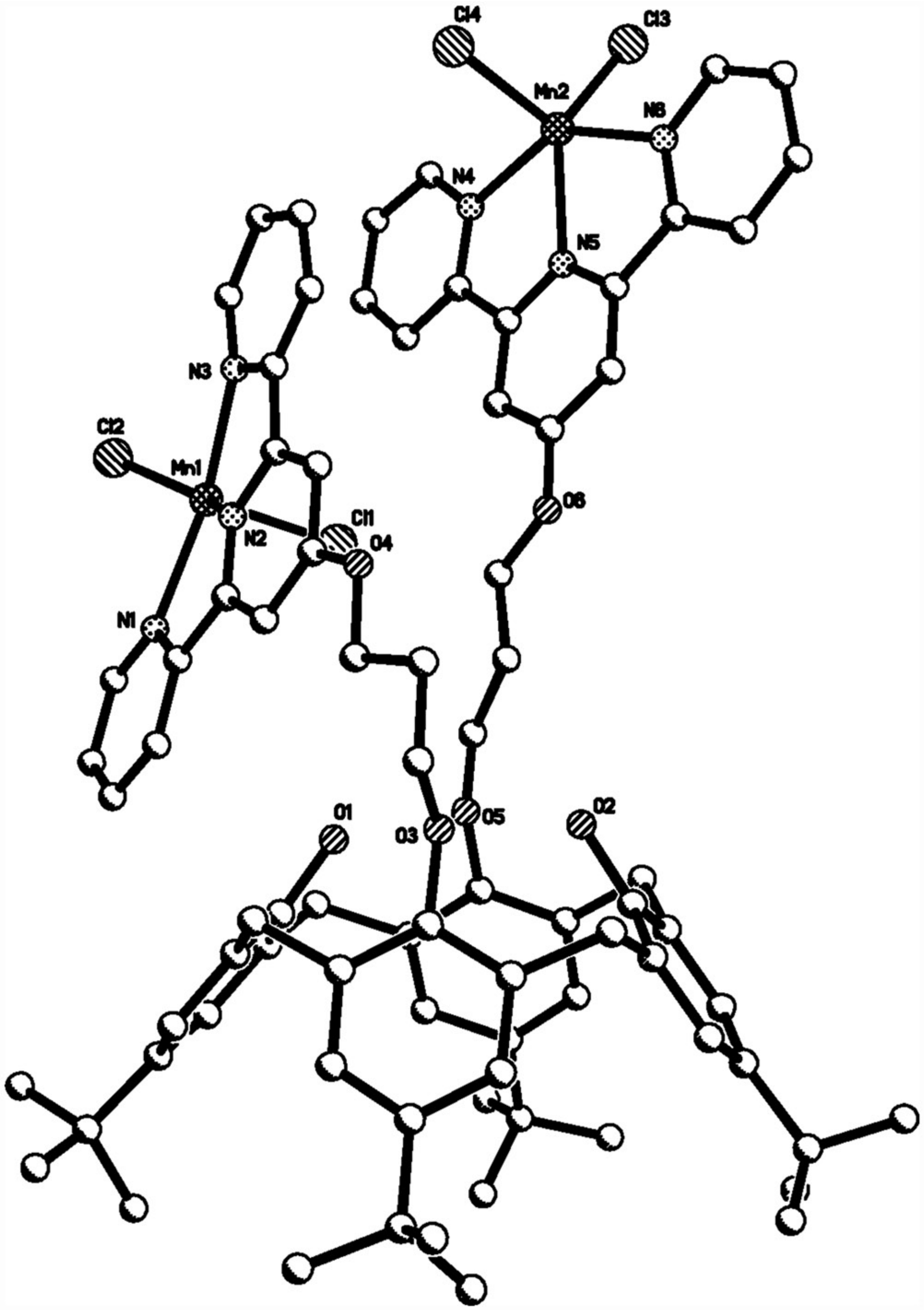


Figure 3. Molecular structure of **2a-Mn**.

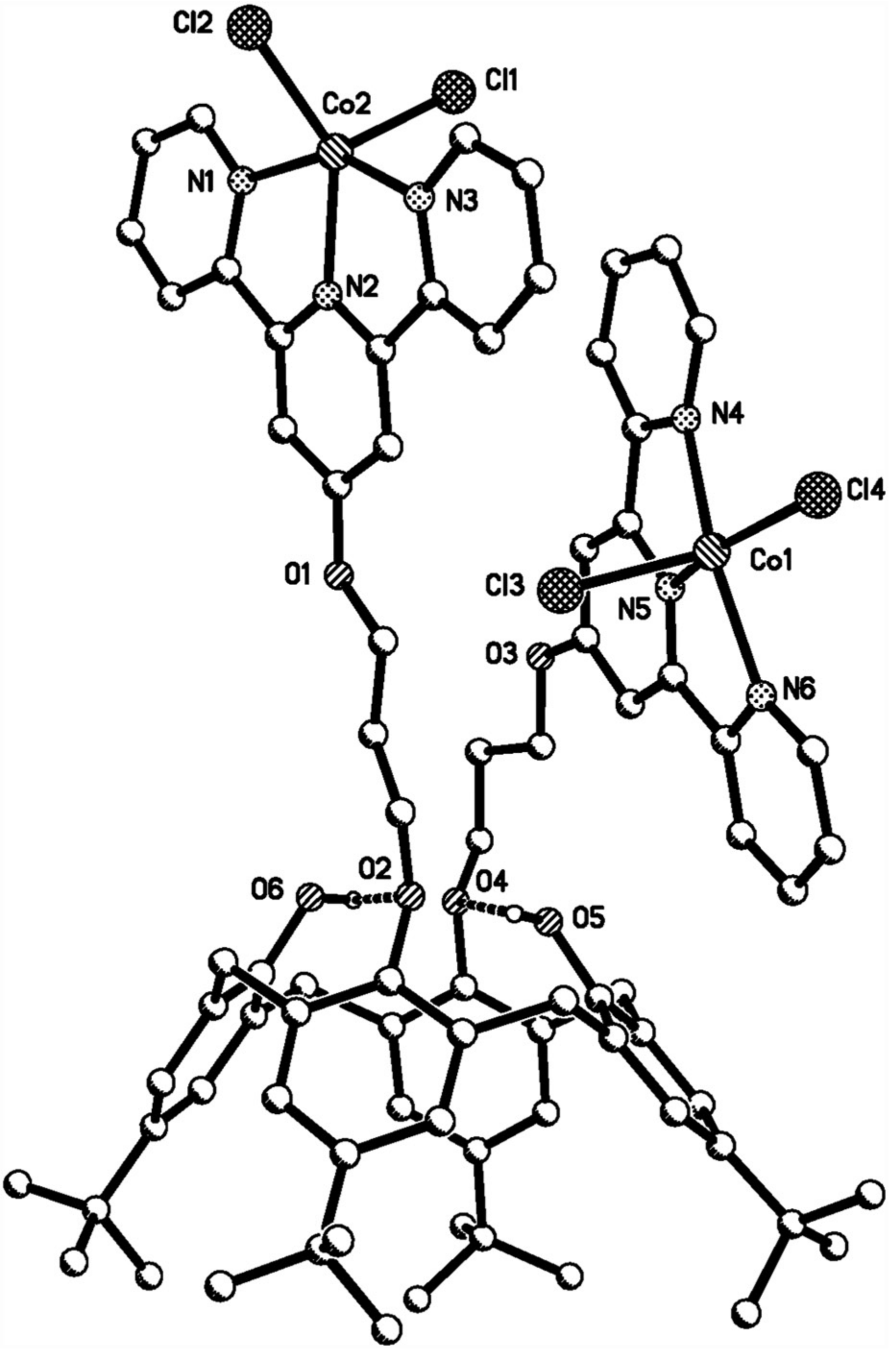


Figure 4. Molecular structure of **2a-Co**.

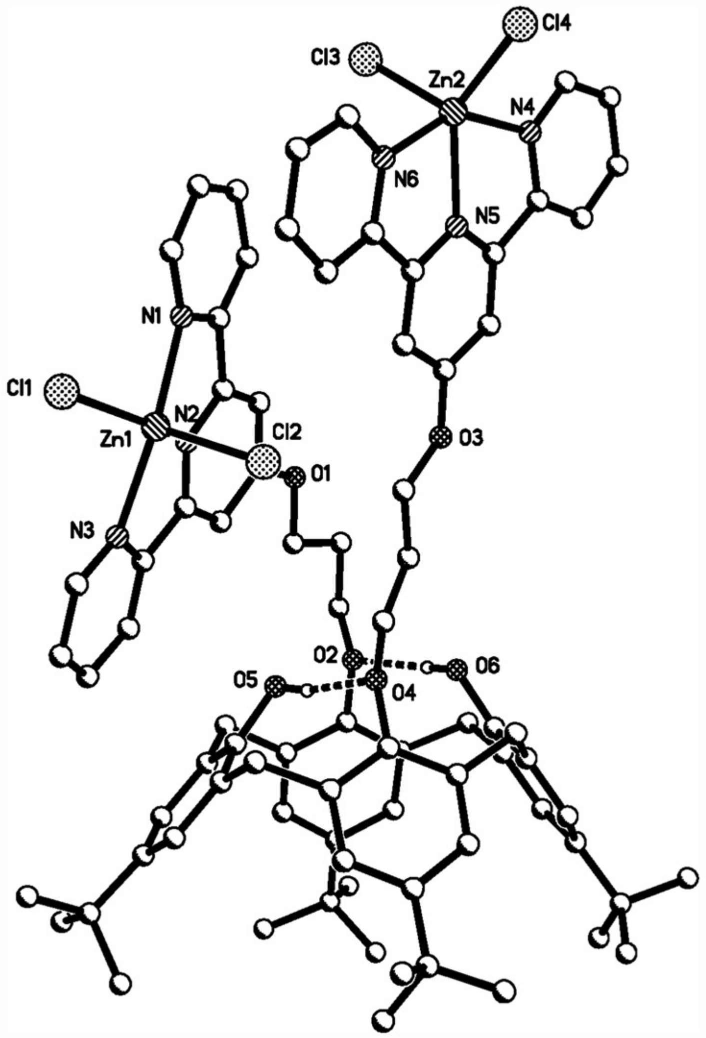


Figure 5. Molecular structure of **2a-Zn**.

to [$MCl_2(terpy)_2$]. The five-coordinate geometry around each metal is either distorted square pyramidal or distorted trigonal bipyramidal.

Complex **2a-Mn** crystallizes in the monoclinic space group *P*21/*c*. As depicted in figure 3, each Mn^{2+} is coordinated to two chloride atoms and three nitrogen atoms of terpyridyl, arranged in a distorted trigonal-bipyramidal geometry. The bond lengths from the central pyridyl nitrogen to manganese [Mn1–N2 2.199(3) Å, Mn2–N5 2.186(4) Å] are shorter than those from the two distal pyridyl rings [Mn1–N1 (2.262(4) Å), Mn1–N3 (2.273(4) Å), Mn2–N4 (2.263(4) Å), Mn2–N6 (2.265(4) Å), similar to reported Mn(terpy)(X_2) complexes [22]. The three pyridyl rings in each terpyridyl also slightly deviate from co-planarity with dihedral angles between adjacent pyridyl rings of 6.16, 7.50 and 6.97, 5.22, respectively.

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

Lengths/angles		**2a-Mn**		**2a-Co**		**2a-Zn**	
M1–N2	M2–N5	2.199(3)	2.186(4)	2.031(3)	2.070(3)	2.102(2)	2.095(2)
M1–N1	M2–N4	2.262(4)	2.263(4)	2.138(3)	2.163(3)	2.210(2)	2.207(3)
M1–N3	M2–N6	2.273(4)	2.265(4)	2.158(3)	2.170(3)	2.200(2)	2.198(2)
M1–Cl1	M1–Cl2	2.3715(13)	2.3410(12)	2.2774(12)	2.2802(11)	2.2556(8)	2.2902(8)
M2–Cl3	M2–Cl4	2.3474(14)	2.3308(16)	2.3234(11)	2.2756(11)	2.2560(9)	2.2618(8)
N1–M1–N2	N4–M2–N5	71.85(12)	71.93(15)	74.53(11)	76.04(11)	73.87(8)	74.43(10)
N1–M1–N3	N4–M2–N6	139.37(12)	143.45(18)	143.82(11)	151.70(12)	144.19(8)	148.42(9)
N2–M1–N3	N5–M2–N6	71.38(12)	72.02(17)	75.04(11)	76.04(11)	74.28(8)	74.48(9)
Cl1–M1–N1	Cl3–M2–N4	98.63(10)	102.69(10)	103.43(8)	98.24(9)	97.70(6)	99.09(7)
Cl1–M1–N2	Cl3–M2–N5	99.47(9)	137.48(11)	92.98(8)	113.81(8)	146.41(6)	113.10(7)
Cl1–M1–N3	Cl3–M2–N6	103.87(9)	99.64(12)	97.22(8)	96.90(8)	99.77(6)	98.01(6)
Cl2–M1–N1	Cl4–M2–N4	103.15(9)	98.91(11)	98.67(9)	97.39(8)	103.28(6)	98.02(7)
Cl2–M1–N2	Cl4–M2–N5	147.63(9)	112.56(10)	156.22(9)	136.80(9)	100.53(6)	135.45(7)
Cl2–M1–N3	Cl4–M2–N6	98.66(9)	100.19(12)	101.31(9)	99.93(8)	98.23(6)	100.14(6)
Cl1–M1–Cl2	Cl3–M1–Cl4	112.88(5)	109.95(6)	110.80(4)	109.38(4)	113.06(3)	111.45(3)

Complex **2a-Co** crystallizes in the monoclinic space group *P*21/*c*. As depicted in figure 4, each terpyridyl coordinates to one Co^{2+}, causing a (1 : 2) complex. Each cobalt is five-coordinate by three nitrogen atoms from a terpyridine unit and two chloride atoms. The coordination geometry of cobalt ion is distorted trigonal bipyramidal, in which N(1) and N(3) occupy two apical positions and Cl(1), Cl(2), and N(2) form the trigonal plane. The N(1)–Co(1)–N(2) and N(2)–Co–N(3) angles are 71.85(12)° and 71.38(12)°, respectively. The same coordination geometry is formed to the secondary cobalt. Similar to other cobalt–terpyridine metal complexes [20], pyridyl nitrogen–cobalt distances are asymmetrical with the central pyridyl nitrogen to cobalt Co2–N2 (2.031(3) Å), Co1–N5 (2.070(3) Å) slightly shorter than those from the two distal pyridyl rings Co1–N6 (2.138(3) Å), Co1–N4 (2.158(3) Å), Co2–N3 (2.163(3) Å), Co2–N1 (2.170(3) Å). The three pyridyl rings in each terpyridyl unit slightly deviate from co-planarity. The dihedral angles between adjacent pyridyl rings are 7.42°, 3.73°, 4.51°, and 2.89°, respectively.

[$Zn2(L2a)Cl_2$] crystallizes in the monoclinic space group *P*21/*c*. In the complex (figure 5), each zinc(II) is distorted trigonal bipyramidal with a tridentate terpyridyl unit and two chloride atoms. The Zn–N bond length is similar to those reported [21] with Zn–N bond length to the central pyridyl ring (2.102(2), 2.095(2) Å) shorter than those to the terminal pyridyl rings (2.210(2), 2.200(2), 2.207(3), 2.198(2) Å). The terpyridyl units are approximately planar with dihedral angles between adjacent pyridyl rings of 6.16°, 7.50°, 6.97°, and 5.22°, respectively.

4. Conclusion

We have developed an efficient protocol for the synthesis of the 1,3-diterpyridyl-substituted *p*-*tert*-butylcalix[4]arenes. This functionalized ligand coordinated with transition metal ions to form complexes on the calixarene platform. X-ray single-crystal diffraction of Mn(II), Co(II), and Zn(II) complexes shows that terpyridyl on calix[4]arene is a tridentate ligand and two chloride atoms coordinate to one metal ion in a distorted trigonal-bipyramidal geometry.

Supplementary material

Crystallographic data (**1a** CCDC 860944, **2a** CCDC 860942, **2a-Mn** CCDC 860945, **2a-Co** CCDC 860946, **2a-Zn** CCDC 860943) have been deposited at the Cambridge Crystallographic Database Centre.

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