



Synthesis, Characterization and X-Ray Crystal Structure of Dizinc(II) Complex of Pseudo Calixarene Macrocycle Based on 2,2-Methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,3-Diamino-2-propanol

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Received: 29 August 2014;

Accepted: 10 January 2015;

Published online: 30 March 2015;

AJC-17093

[(2+2)Zn₂-CH₃COO] complex was prepared by refluxing 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] (H₂mftbp) and 1,3-diamino-2-propanol in a round-bottomed flask containing Ca(ClO₄)₂ in ethanol in the presence of a base. Sample was taken from the refluxing solution and submitted for MS. ESI-MS showed the peak to confirm the formation of calcium complex [(2+2)Ca] but when Zn(CH₃COO)₂·2H₂O was added and refluxed for further 6 h. Zinc replaced calcium metal and a new complex of Zn was formed as [Zn₂(2+2)] complex. A yellow powder was filtered after cooling at room temperature. The powder was crystallized by vapour diffusion method. The complex crystallizes in the monoclinic crystal system with space group P2(1)/n. Unit cell parameters are; a = 13.6595(7) Å, b = 18.5216(9) Å, c = 25.0723(12) Å, α = 90°, β = 95.7020(10)°, γ = 90°, Z = 8 and V = 6311.8(5) Å³. The complex was characterized by using single crystal X-ray spectroscopy, IR-spectroscopy and ESI-mass spectrophotometry.

Keywords: 2,2-Methylene-bis[(6-formyl)-4-tert-butylphenol], 1,3-Diamino-2-propanol, Zinc complex, Calixarene.

INTRODUCTION

“Robson type” Schiff base macrocycles containing bridging phenol groups have been extensively used to synthesize homo nuclear and hetro nuclear macrocycles for several years. Detailed investigation of chemistry of dinuclear and polynuclear phenol based macrocyclic systems has enabled important insights in a number of areas, such as magneto-chemistry, site selection, catalytic and bioinorganic model chemistry¹. Expansion to larger macrocycles accommodating polynuclear assemblies has been achieved in the last few years^{2,3}.

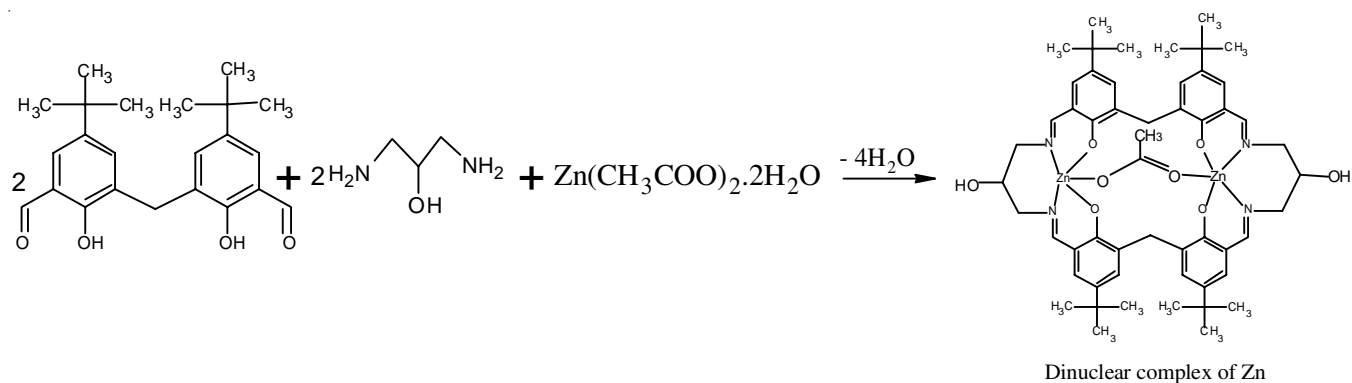
Preparation of cyclic Schiff bases is rather difficult. Different condensation products (polymeric or oligomeric in nature) may be resulted when di- or poly functional precursors are used. This will require another step to purify the desired macrocyclic product and reduces the yield. To overcome this problem, high dilution conditions may be used, in which a large amount of solvent reduces the chances of cross reactions. An alternative way to avoid cross reactions is to use a metal ion in a template reaction. Metal ion is not always necessary for the preparation of Schiff base ligands⁴⁻⁶. Schiff base condensation reactions with metal template ions are one of the most common methods to prepare macrocyclic systems. A metal ion in a template reaction directs the cyclization of a ligand⁷⁻⁹.

EXPERIMENTAL

0.1 g (0.273 mmol) 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] (H₂mftbp) was added in a round-bottomed flask containing 0.0653 g (0.273 mmol) Ca(ClO₄)₂ in 60 mL ethanol. It was refluxed for 0.5 h to dissolve H₂mftbp completely. To this clear solution, 0.0246 g (0.2714 mmol) 1,3-diamino-2-propanol was added and refluxed for 45 min and then to this refluxing solution, 1 mL of Et₃N was added. After refluxing it overnight, 0.06 g (0.2731 mmol) Zn(CH₃COO)₂·2H₂O was added and refluxed for further 6 h. It was filtered after cooling at room temperature to get a yellow powder. This powder was crystallized by vapour diffusion method using DMF and diethyl ether. Yield was 0.078 g.

RESULTS AND DISCUSSION

Synthesis of the precursor 2,2-methylene-bis-[(6-hydroxymethyl)-4-tert-butylphenol] (H₂mhtbp) from *p*-tert-butylphenol is very famous in calixarene chemistry. This precursor can be oxidized, using manganese dioxide, to 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] (H₂mftbp). Dinuclear complex of zinc was synthesized by refluxing 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] (H₂mftbp) and 1,3-diamino-2-propanol in a round-bottomed flask containing



Ca(ClO₄)₂ in 60 mL ethanol in the presence of a base. Sample was taken from the refluxing solution and submitted for MS. ESI-MS scan showed a singly charged peak at m/z 923.5670 [(2+2)Ca₂]⁺¹ that indicates the presence of calcium complex of [(2+2) macrocycle with molecular formula C₅₂H₆₈N₄O₆Ca₂. But when Zn(CH₃COO)₂·2H₂O was added and refluxed for further 6 h, Zn replaced Ca metal and a new complex of Zn was formed as [Zn₂(2+2)] complex. A yellow powder was filtered after cooling at room temperature. This powder was crystallized by vapour diffusion method using DMF and diethyl ether. The complex crystallizes in the monoclinic crystal system with space group P 2(1)/n. Unit cell parameters are; $a = 13.6595(7)$ Å, $b = 18.5216(9)$ Å, $c = 25.0723(12)$ Å, $\alpha = 90^\circ$, $\beta = 95.7020(10)^\circ$, $\gamma = 90^\circ$, $Z = 8$ and $V = 6311.8(5)$ Å³. Unit cell has Z value 8, *i.e.* unit cell contains 8 mol of dinuclear complex of zinc. Dinuclear complex of zinc is shown in Figs. 1-3. Each zinc ion is coordinated to two imine groups, two phenol oxygen atoms and a bridging acetate ion. Geometry around each metal cation is square pyramidal with acetate oxygen at apical. Two hydrogen bond linkages are present between adjacent phenol oxygen atoms as shown in Fig. 1. Presence of hydrogen bonds indicates that one proton is lost from each pair of phenols. Alcohol groups are not involved in bonding to zinc ions. The macrocycle adopts a saddle conformation with adjacent phenolic rings inclined at 68.5(1)° and 68.7(1)° as shown in Fig. 2.

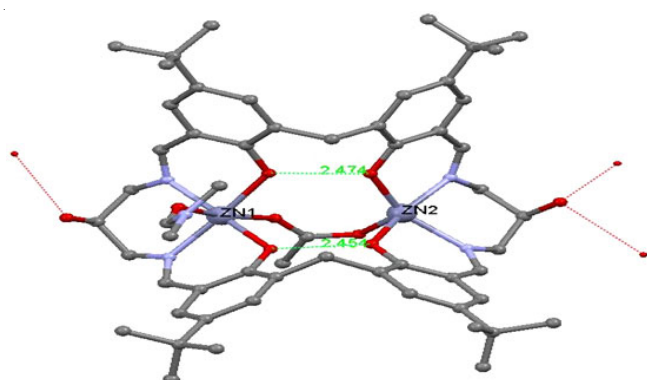


Fig. 1.

In ESI-MS scan (Fig. 4) (m/z , rel. intensity, assignment), a singly charged peak at m/z 1051.7992 confirms the formation of [Zn₂(2+2)(CH₃COO)(NH₄)⁺¹]⁺¹. It means that two molecules of 2,2-methylene-bis[(6-formyl)-4-*tert*-butylphenol] and two molecules of 1,3-diamino-2-propanol make a (2+2) macrocycle

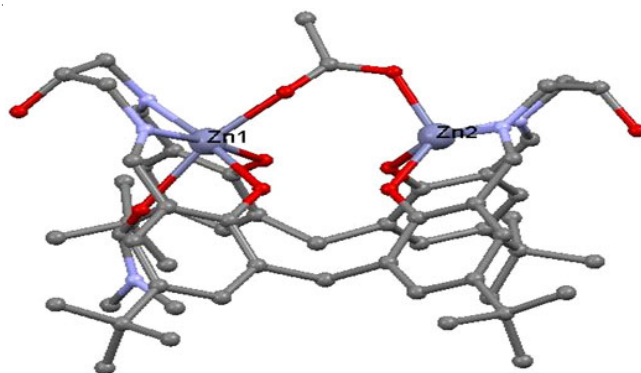


Fig. 2.

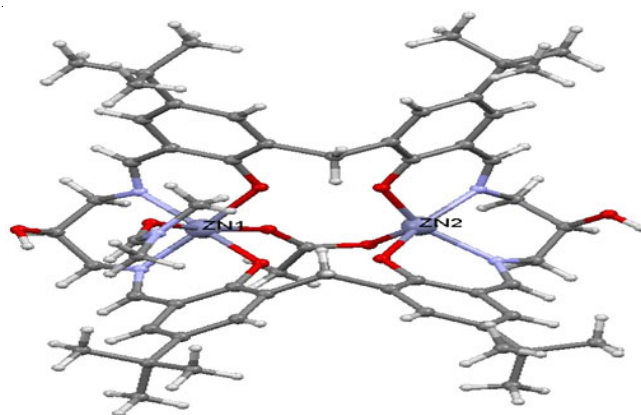


Fig. 3

to make dinuclear complex with zinc and zinc acts as a template to make macrocycle by Schiff-base condensation reaction rather than an oily product.

IR spectra (Fig. 5) also confirmed the successful synthesis of macrocycle. A stretching band at 1627.37 cm⁻¹ indicates the presence of (-N=C-) imine bond and ensures Schiff-base condensation reaction. Similarly a peak at 3435.89 cm⁻¹ shows the presence of (-OH) and confirms the presence of hydrogen bond. Other peaks found in scan are 2955.92, 2902.12, 1563.55, 1463.35, 1400.92, 1361.18, 1322.73, 1271.15, 1212.93, 1121.05, 1019.69, 875.50, 828.40, 802.78, 748.94, 661.87 and 618.40 cm⁻¹.

Single-crystal X-ray analysis: Structure determination and refinement was done on a Bruker Smart Apex II diffractometer using MoK_α radiation ($k = 0.71073$ Å). The APEX2^{10,11} program package was used for cell refinements and data reductions. The structure was solved by direct methods using

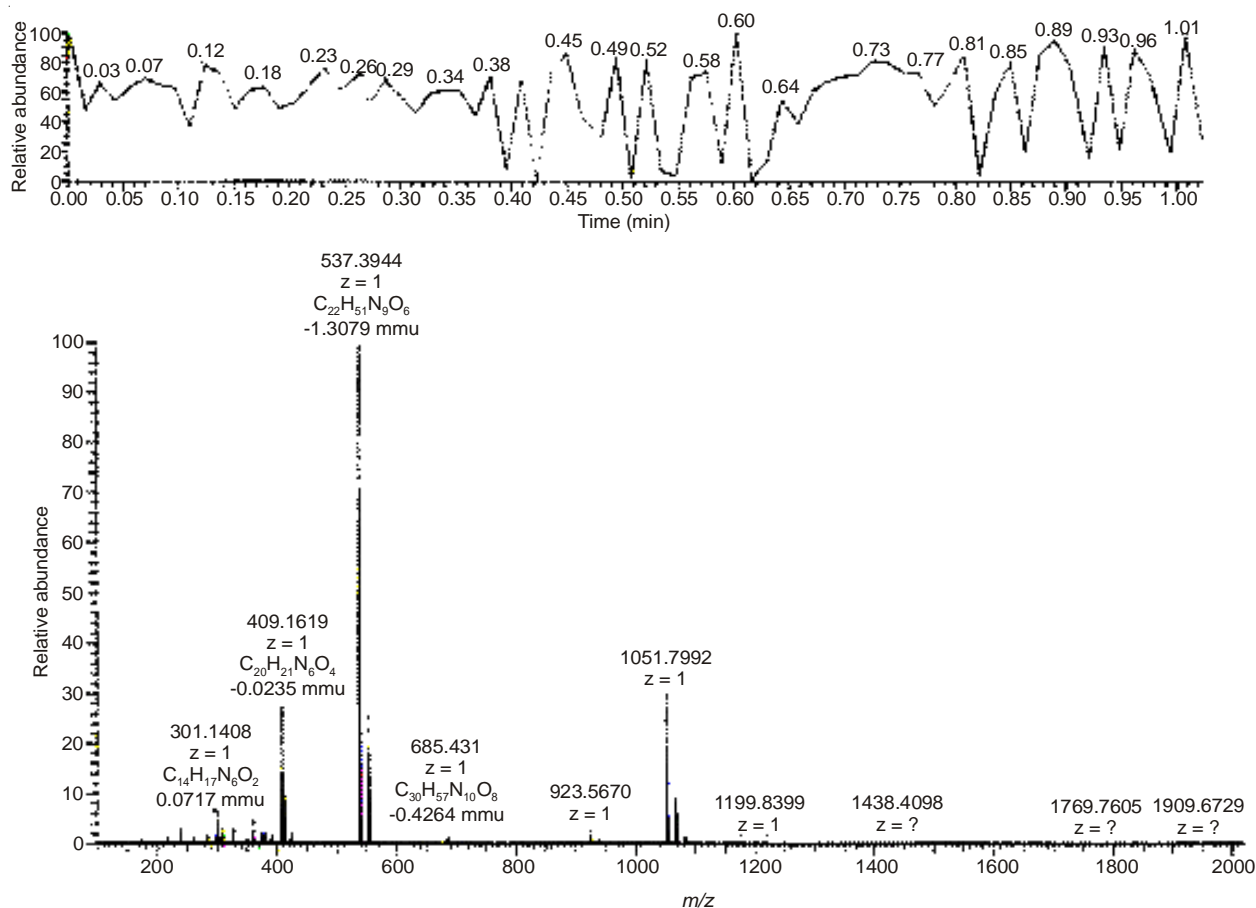


Fig. 4. ESI-MS-Scan of a dinuclear complex of zinc with a macrocycle based on 2,2-methylene-bis[(6-formyl)-4-*tert*-butylphenol] and 1,3-diamino-2-propanol

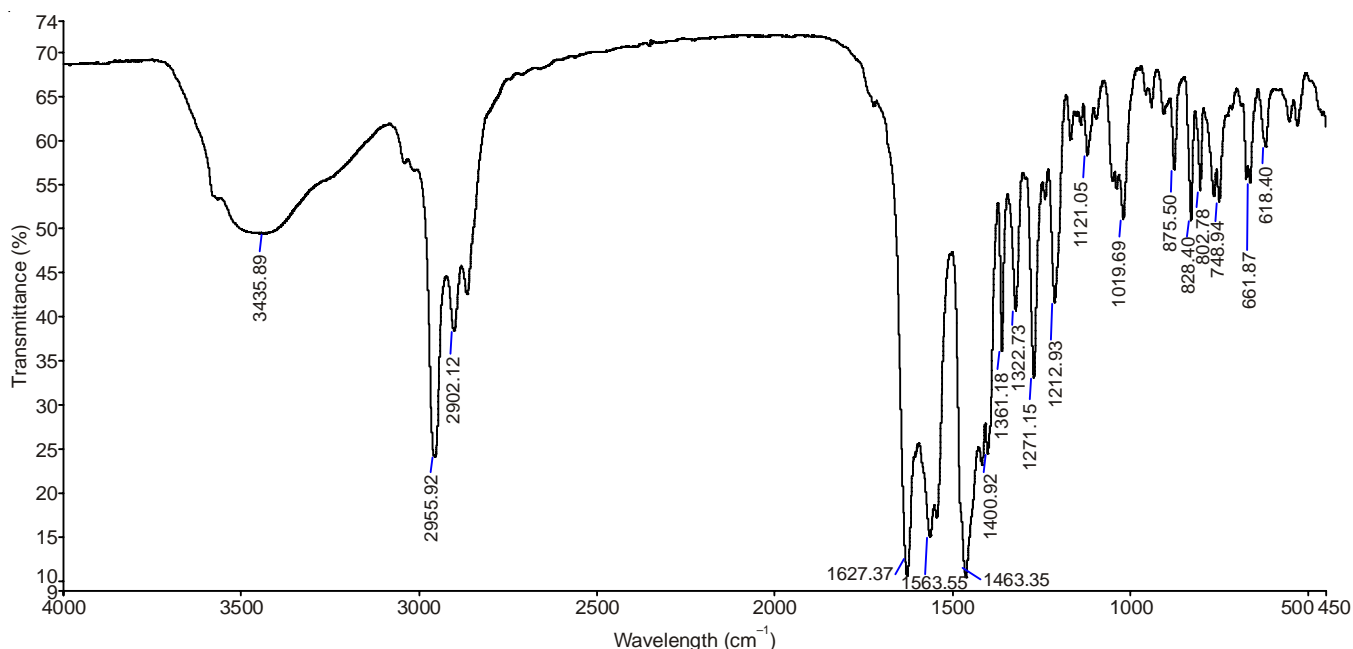


Fig. 5. IR-scan of a dinuclear complex of zinc with a macrocycle based on 2,2-methylene-bis[(6-formyl)-4-*tert*-butylphenol] and 1,3-diamino-2-propanol

SHELXL-2012¹² with the WinGX¹³ graphical user interface. An empirical absorption correction (SADABS)¹⁴ was applied to the data. Structural refinements were carried out using SHELXL-97^{15,16}. All the non-hydrogen atoms were refined

using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Crystallographic data is shown in Tables 1-3.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR SYNTHESIZED DIZINC COMPLEX

Identification code	sad-sr	Crystal description	? ?
Empirical formula	C _{28.50} H ₃₇ N _{2.50} O _{6.50} ZnCl _{0.50}	Crystal size	0.39 mm × 0.23 mm × 0.20 mm
Formula weight	601.70	Theta range for data collection	1.37 to 28.34°
Temperature	150(2) K	Index ranges	-18<=h<=18; -24<=k<=24, -33<=l<=33
Wavelength	0.71073 Å	Reflections collected	64708
Crystal system	Monoclinic	Independent reflections	15724 [R(int) = 0.0403]
Space group	P2(1)/n	Completeness to $\theta = 28.34^\circ$	99.7 %
Unit cell dimensions	a = 13.6595(7) Å; $\alpha = 90^\circ$ b = 18.5216(9) Å; $\beta = 95.7020(10)^\circ$ c = 25.0723(12) Å; $\gamma = 90^\circ$	Absorption correction	Semi-empirical from equivalents
Volume	6311.8(5) Å ³	Max. and min. transmission	0.8463 and 0.7295
Z	8	Refinement method	Full-matrix least-squares on F ²
Density (calculated)	1.266 Mg/m ³	Data/restraints/parameters	15724/0/720
Absorption coefficient	0.863 mm ⁻¹	Goodness-of-fit on F ²	1.091
F(000)	2528	Final R indices [I>2 σ (I)]	R1 = 0.0610, wR2 = 0.1808
		R indices (all data)	R1 = 0.0789, wR2 = 0.1915
		Largest diff. peak and hole	2.617 and -0.732 e. Å ⁻³

TABLE-2
BOND LENGTHS (Å) AND ANGLES (°) FOR SYNTHESIZED DIZINC COMPLEX

Zn(1)-O(5)	2.006(2)	C(13)-C(14)	1.391(4)	N(4)-Zn(1)-O(1)	174.11(10)	C(4)-C(3)-C(2)	122.2(3)
Zn(1)-N(1)	2.050(3)	C(13)-C(18)	1.409(4)	O(5)-Zn(1)-O(9)	85.99(10)	C(3)-C(4)-C(5)	116.6(3)
Zn(1)-O(7)	2.085(2)	C(14)-C(15)	1.402(4)	N(1)-Zn(1)-O(9)	87.43(10)	C(3)-C(4)-C(8)	123.6(3)
Zn(1)-N(4)	2.103(3)	C(15)-C(16)	1.386(5)	O(7)-Zn(1)-O(9)	166.84(13)	C(5)-C(4)-C(8)	119.8(3)
Zn(1)-O(1)	2.108(2)	C(15)-C(19)	1.535(4)	N(4)-Zn(1)-O(9)	91.18(12)	C(6)-C(5)-C(4)	123.1(3)
Zn(1)-O(9)	2.361(3)	C(16)-C(17)	1.412(4)	O(1)-Zn(1)-O(9)	82.96(11)	C(5)-C(6)-C(7)	119.0(3)
Zn(2)-O(8)	1.992(2)	C(17)-C(18)	1.415(4)	O(8)-Zn(2)-O(2)	120.96(10)	C(5)-C(6)-C(12)	120.3(3)
Zn(2)-O(2)	2.0354(19)	C(17)-C(23)	1.439(4)	O(8)-Zn(2)-N(2)	102.63(11)	C(7)-C(6)-C(12)	120.7(2)
Zn(2)-N(2)	2.074(3)	C(19)-C(21)	1.498(6)	O(2)-Zn(2)-N(2)	86.84(9)	O(1)-C(7)-C(6)	120.4(2)
Zn(2)-N(3)	2.090(3)	C(19)-C(22)	1.528(6)	O(8)-Zn(2)-N(3)	94.53(11)	O(1)-C(7)-C(2)	119.9(2)
Zn(2)-O(4)	2.104(2)	C(19)-C(20)	1.547(6)	O(2)-Zn(2)-N(3)	144.22(10)	C(6)-C(7)-C(2)	119.7(2)
Cl(1)-O(12)	1.360(5)	C(24)-C(25)	1.535(5)	N(2)-Zn(2)-N(3)	89.79(10)	C(10)-C(8)-C(11)	109.3(3)
Cl(1)-O(11)	1.381(4)	C(25)-C(26)	1.516(5)	O(8)-Zn(2)-O(4)	97.54(10)	C(10)-C(8)-C(4)	112.0(3)
Cl(1)-O(10)	1.401(5)	C(27)-C(28)	1.459(4)	O(2)-Zn(2)-O(4)	85.46(8)	C(11)-C(8)-C(4)	109.1(3)
Cl(1)-O(13)	1.402(7)	C(28)-C(29)	1.402(4)	N(2)-Zn(2)-O(4)	159.58(10)	C(10)-C(8)-C(9)	107.6(3)
N(1)-C(1)	1.285(4)	C(28)-C(33)	1.407(4)	N(3)-Zn(2)-O(4)	85.49(9)	C(11)-C(8)-C(9)	109.0(3)
N(1)-C(52)	1.465(4)	C(29)-C(30)	1.390(4)	O(12)-Cl(1)-O(11)	119.2(4)	C(4)-C(8)-C(9)	109.8(2)
N(2)-C(23)	1.288(4)	C(30)-C(31)	1.400(4)	O(12)-Cl(1)-O(10)	112.2(5)	C(6)-C(12)-C(13)	113.4(2)
N(2)-C(24)	1.467(4)	C(30)-C(34)	1.537(4)	O(11)-Cl(1)-O(10)	109.8(3)	C(14)-C(13)-C(18)	119.9(3)
N(3)-C(27)	1.276(4)	C(31)-C(32)	1.385(4)	O(12)-Cl(1)-O(13)	102.4(6)	C(14)-C(13)-C(12)	119.6(3)
N(3)-C(26)	1.477(4)	C(32)-C(33)	1.395(4)	O(11)-Cl(1)-O(13)	107.9(4)	C(18)-C(13)-C(12)	120.5(2)
N(4)-C(49)	1.273(4)	C(32)-C(38)	1.515(4)	O(10)-Cl(1)-O(13)	103.7(5)	C(13)-C(14)-C(15)	123.4(3)
N(4)-C(50)	1.470(4)	C(34)-C(35)	1.439(7)	C(1)-N(1)-C(52)	117.1(3)	C(16)-C(15)-C(14)	116.1(3)
N(5)-C(55)	1.329(6)	C(34)-C(37)	1.484(8)	C(1)-N(1)-Zn(1)	124.9(2)	C(16)-C(15)-C(19)	123.3(3)
N(5)-C(57)	1.426(6)	C(34)-C(36)	1.528(6)	C(52)-N(1)-Zn(1)	117.98(19)	C(14)-C(15)-C(19)	120.6(3)
N(5)-C(56)	1.444(5)	C(38)-C(39)	1.515(4)	C(23)-N(2)-C(24)	116.5(3)	C(15)-C(16)-C(17)	122.8(3)
O(1)-C(7)	1.362(3)	C(39)-C(40)	1.392(4)	C(23)-N(2)-Zn(2)	125.6(2)	C(16)-C(17)-C(18)	119.7(3)
O(2)-C(18)	1.332(3)	C(39)-C(44)	1.405(4)	C(24)-N(2)-Zn(2)	117.3(2)	C(16)-C(17)-C(23)	116.2(3)
O(3)-C(25)	1.399(5)	C(40)-C(41)	1.396(4)	C(27)-N(3)-C(26)	115.9(3)	C(18)-C(17)-C(23)	124.1(3)
O(4)-C(33)	1.367(3)	C(41)-C(42)	1.394(4)	C(27)-N(3)-Zn(2)	127.0(2)	O(2)-C(18)-C(13)	119.9(3)
O(5)-C(44)	1.342(3)	C(41)-C(45)	1.533(4)	C(26)-N(3)-Zn(2)	116.9(2)	O(2)-C(18)-C(17)	122.0(3)
O(6)-C(51)	1.385(4)	C(42)-C(43)	1.402(4)	C(49)-N(4)-C(50)	117.4(3)	C(13)-C(18)-C(17)	118.1(3)
O(7)-C(53)	1.240(4)	C(43)-C(44)	1.410(4)	C(49)-N(4)-Zn(1)	122.2(2)	C(21)-C(19)-C(22)	110.1(4)
O(8)-C(53)	1.251(4)	C(43)-C(49)	1.461(4)	C(50)-N(4)-Zn(1)	120.0(2)	C(21)-C(19)-C(15)	112.8(3)
O(9)-C(55)	1.219(5)	C(45)-C(46)	1.519(4)	C(55)-N(5)-C(57)	122.6(4)	C(22)-C(19)-C(15)	109.2(3)
C(1)-C(2)	1.462(4)	C(45)-C(47)	1.534(5)	C(55)-O(7)-Zn(1)	119.0(4)	C(21)-C(19)-C(20)	108.0(4)
C(2)-C(7)	1.398(4)	C(45)-C(48)	1.549(5)	C(57)-N(5)-C(56)	118.4(4)	C(22)-C(19)-C(20)	108.2(4)
C(2)-C(3)	1.415(4)	C(50)-C(51)	1.524(5)	C(7)-O(1)-Zn(1)	122.89(17)	C(15)-C(19)-C(20)	108.4(3)
C(3)-C(4)	1.381(4)	C(51)-C(52)	1.531(5)	C(18)-O(2)-Zn(2)	127.90(18)	N(2)-C(23)-C(17)	127.0(3)
C(4)-C(5)	1.403(4)	O(5)-Zn(1)-N(1)	173.34(9)	C(33)-O(4)-Zn(2)	128.61(17)	N(2)-C(24)-C(25)	111.1(3)
C(4)-C(8)	1.538(4)	O(5)-Zn(1)-O(7)	87.98(10)	C(44)-O(5)-Zn(1)	120.60(17)	O(3)-C(25)-C(26)	113.4(3)
C(5)-C(6)	1.392(4)	N(1)-Zn(1)-O(7)	98.23(10)	C(53)-O(7)-Zn(1)	145.9(2)	O(3)-C(25)-C(24)	108.1(3)
C(6)-C(7)	1.396(4)	O(5)-Zn(1)-N(4)	86.76(9)	C(53)-O(8)-Zn(2)	124.4(2)	C(26)-C(25)-C(24)	113.0(3)
C(6)-C(12)	1.516(4)	N(1)-Zn(1)-N(4)	94.45(10)	C(55)-O(9)-Zn(1)	140.1(3)	N(3)-C(26)-C(25)	115.2(3)
C(8)-C(10)	1.531(5)	O(7)-Zn(1)-N(4)	100.16(11)	N(1)-C(1)-C(2)	126.7(3)	N(3)-C(27)-C(28)	127.6(3)
C(8)-C(11)	1.533(5)	O(5)-Zn(1)-O(1)	93.34(8)	C(7)-C(2)-C(3)	119.3(3)	C(29)-C(28)-C(33)	119.1(3)
C(8)-C(9)	1.539(4)	N(1)-Zn(1)-O(1)	84.79(9)	C(7)-C(2)-C(1)	123.9(3)	C(29)-C(28)-C(27)	115.8(3)
C(12)-C(13)	1.524(4)	O(7)-Zn(1)-O(1)	85.72(10)	C(3)-C(2)-C(1)	116.8(3)	C(33)-C(28)-C(27)	125.1(3)

C(30)-C(29)-C(28)	122.7(3)	C(35)-C(34)-C(36)	110.4(6)	C(40)-C(41)-C(45)	123.3(3)	C(41)-C(45)-C(48)	111.4(3)
C(29)-C(30)-C(31)	116.2(3)	C(37)-C(34)-C(36)	101.9(6)	C(41)-C(42)-C(43)	122.3(3)	C(47)-C(45)-C(48)	108.0(3)
C(29)-C(30)-C(34)	121.6(3)	C(35)-C(34)-C(30)	110.1(3)	C(42)-C(43)-C(44)	119.7(3)	N(4)-C(49)-C(43)	126.3(3)
C(31)-C(30)-C(34)	122.2(3)	C(37)-C(34)-C(30)	111.2(4)	C(42)-C(43)-C(49)	116.8(3)	N(4)-C(50)-C(51)	112.6(3)
C(32)-C(31)-C(30)	123.2(3)	C(36)-C(34)-C(30)	109.6(3)	C(44)-C(43)-C(49)	123.4(3)	O(6)-C(51)-C(50)	111.3(3)
C(31)-C(32)-C(33)	119.5(3)	C(39)-C(38)-C(32)	113.5(2)	O(5)-C(44)-C(39)	119.8(3)	O(6)-C(51)-C(52)	111.3(3)
C(31)-C(32)-C(38)	118.8(3)	C(40)-C(39)-C(44)	119.6(3)	O(5)-C(44)-C(43)	121.5(3)	C(50)-C(51)-C(52)	114.9(3)
C(33)-C(32)-C(38)	121.7(3)	C(40)-C(39)-C(38)	120.4(3)	C(39)-C(44)-C(43)	118.7(3)	N(1)-C(52)-C(51)	113.1(3)
O(4)-C(33)-C(32)	120.8(2)	C(44)-C(39)-C(38)	119.9(2)	C(46)-C(45)-C(41)	109.5(3)	O(7)-C(53)-O(8)	124.5(3)
O(4)-C(33)-C(28)	119.9(3)	C(39)-C(40)-C(41)	122.9(3)	C(46)-C(45)-C(47)	108.7(3)	O(7)-C(53)-C(54)	117.9(4)
C(32)-C(33)-C(28)	119.3(3)	C(42)-C(41)-C(40)	116.7(3)	C(41)-C(45)-C(47)	110.0(3)	O(8)-C(53)-C(54)	117.6(3)
C(35)-C(34)-C(37)	113.3(7)	C(42)-C(41)-C(45)	120.0(3)	C(46)-C(45)-C(48)	109.2(3)	O(9)-C(55)-N(5)	124.6(5)

TABLE-3
HYDROGEN BONDS FOR SYNTHESIZED DIZINC COMPLEX (Å AND °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
O(3)-H(3)...O(11)	0.84	2.16	2.992(6)	170.6

Symmetry transformations used to generate equivalent atoms.

Conclusion

This macrocycle makes more stable complex with zinc than calcium. Because it is clear from mass spectroscopic study that zinc replaced calcium metal ion from the complex. Protonation level of methylenediphenol units control the conformations of dinuclear complex and the protonation level depends on oxidation state of metal ions. In this complex strong O-H-O interactions hold macrocycle in a saddle shaped conformation. Intramolecular hydrogen bond is present between adjacent phenol oxygen atoms.

ACKNOWLEDGEMENTS

The authors highly thankful to Dr. Rubina Gillani for her guidance, Higher Education Commission of Pakistan for providing financial support. Prof. Vickie McKee and School of Chemistry, Loughborough University, Loughborough, UK to help to complete this research project and for running Single Crystal X-Ray to predict the crystal structure of synthesized macrocycle. One of the authors (I.H.) also thankful to Dr. Muhammet Kose for helping in research in the laboratory.

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