

Pendant-armed Unsymmetrical Aza-macrocycles: Syntheses, Coordination Behavior and Crystal Structure of a Dinuclear Cadmium Complex

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Two unsymmetrical tetradentate aza-macrocycles with side arms attached to the N_{sp^3} atoms, L^1 and L^2 , as well as their complexes with different metal cations were synthesized and characterized by EA, UV, IR, 1H NMR and MS spectra. Both the two ligands can efficiently transport alkali and transition metal cations across an organic membrane with high selectivity ratio. The structure of a dinuclear Cd(II) complex $[L^1 \cdot (Cd-Cl_2)_2]$ was elucidated by X-ray crystallography and was solved by the heavy-atom method to a final R value of 0.029 for 3084 reflections with $|F| > 3\sigma(I)$. In the exo-structure of the dinuclear complex each cadmium atom is five-coordinated, bonding to three N atoms and two chlorine atoms.

Keywords synthesis, coordination, macrocycle, complex, transport

Introduction

In some biological studies it has been demonstrated that the complexation of functional groups that are integral parts of the structure but not fixed rigidly in place, provides a mechanism for activation of the metal sites.^{1,2} Receptors in living systems usually contain different types of donor atom whose interactions with various substrates are difficult to predict. Most of the macrocycles with mixed donor sites have shown very interesting behavior in metal ion discrimination because of the occurrence of dislocation phenomena.³ There has been therefore considerable interest in the chemistry of metal complexes involving macro-

cyclic ligands with pendant arms.⁴ Tetraazamacrocycles containing pendant coordinating groups attached to the nitrogen atoms have been suggested as ditopic ligands for dinuclear metal complexes.⁵⁻⁷ Moore and co-workers⁶ reported the syntheses of the ligand 1,4,8,11-tetrakis[2-pyridylmethyl]-1,4,8,11-tetraazacyclotetradecane and the corresponding copper(II) complexes which are dinuclear with two copper atoms coordinated outside the macrocyclic cavity while in the rhenium complex only three of the N atoms from the macrocyclic ring are coordinated. In the present paper, the syntheses of two new unsymmetrical tetraazamacrocycles, incorporating sp^2 and sp^3 nitrogen atoms as donor sites and with two functional groups as pendant arms attached on the N_{sp^3} atoms, L^1 and L^2 , were reported together with their complexing behavior with some metal cations and abilities for transporting metal cations across organic membrane. The crystal structure of the 1:2 type Cd(II) complex of L^1 has been determined and described.

Results and discussion

Syntheses of ligands

The synthetic procedure of two macrocyclic ligands, L^1 and L^2 , is outlined in Scheme 1. Using 3-methoxycarbonyl-5-methyl pyrazole as precursor, 1,4-bis(3'-chloromethyl-5'-methyl-1'-pyrazolyl)butane (**2**) was prepared

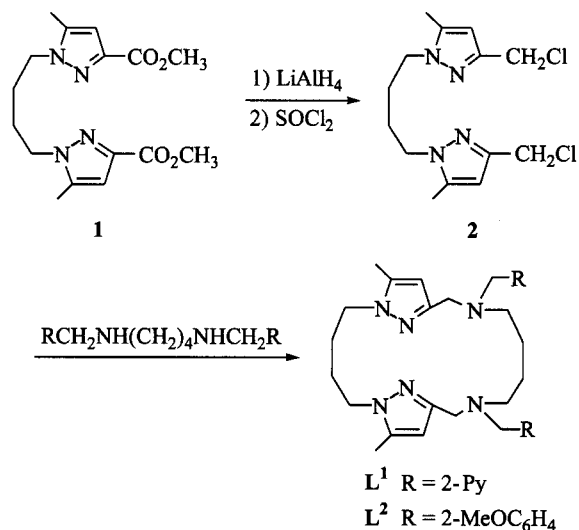
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through three steps as described in our earlier work.^{8,9} **L**¹ and **L**² were prepared by cyclo-condensation of the dichloro-compound with different diamino-compounds under dilution conditions in 40%—50% yield.

Scheme 1



Preparation of complexes

The preparation of complexes of the macrocyclic ligands obtained above shows that both **L**¹ and **L**² can form thermostable complexes with alkali or transition metal ions, but the ratio of the complex formation is different. They can form 1:1 type complexes with K^+ but the corresponding Na^+ complex is not stable, indicating that the ring size of the ligands is more appropriate for potassium ion. **L**¹ can form 1:2 type complex with Cd^{2+} , whereas only 1:1 type Cd complex is obtained for **L**². The crystal structure of the 1:2 type Cd complex of **L**¹ shows that the two Cd^{2+} cations are chelated in two coordinate centers outside the macrocycle. The interesting result that **L**²

formed 2:3 type complex with Co^{2+} indicates that the two MeO groups in the pendent arms may take special role in the complex formation.

Transport of metal cations through a liquid membrane

As an extension of the ability of the ligands to extract and release alkali metal cations, their role as carriers transporting metal ions across a liquid membrane was studied. The transport was carried out through a CH_2Cl_2 membrane separating two aqueous solutions as described previously.¹⁰ The transported salt would be the picrate because of its lipophilic property, which allowed a good incorporation in the organic phase containing the macrocycle studied.¹¹

The carrier abilities of macrocycles **L**¹ and **L**² toward Li^+ , Na^+ , K^+ , Hg^{2+} , Cd^{2+} , Ni^{2+} or Co^{2+} were studied because their complexation properties had been found to be good enough to undertake such experiments. The transport rates and selectivity ratios are given in Table 1.

It is shown from the study that there is no transport of any picrate ion across the membrane in the absence of carrier molecule. Compared with other macrocycles reported in the literatures,^{12,13} both **L**¹ and **L**² show higher transport rates for most of the metal cations studied. The transport rates for alkali metal cations ($\text{K}^+ > \text{Na}^+ > \text{Li}^+$ for both **L**¹ and **L**²) and the high K^+/Li^+ selectivity ratios indicate that the two ligands have good complexing and release abilities for Na^+ and K^+ , but the diameter of K^+ matches the ring size of the ligands better. These results are in accordance with the complexing behavior of the ligands for alkali metal cations. Both **L**¹ and **L**² behave as very good carriers for transporting Hg^{2+} but their selectivity ratios for $\text{Hg}^{2+}/\text{Cd}^{2+}$, $\text{Hg}^{2+}/\text{Ni}^{2+}$ and $\text{Hg}^{2+}/\text{Co}^{2+}$ are not very appreciable.

Table 1 Transport rate values in 10^{-6} mol/h and selectivity ratios

Transport rate	Li^+	Na^+	K^+	Hg^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
	L ¹	1.0	22.6	45.7	78.4	25.0	11.5
L ²	3.4	29.2	58.5	33.3	18.4	9.6	5.8
Selectivity ratio	Na^+/Li^+	K^+/Li^+	K^+/Na^+	$\text{Hg}^{2+}/\text{Cd}^{2+}$	$\text{Hg}^{2+}/\text{Ni}^{2+}$	$\text{Hg}^{2+}/\text{Co}^{2+}$	
	L ¹	22.6	45.7	2.02	3.14	6.82	8.80
L ²	8.59	17.2	2.00	1.81	3.47	5.74	

Crystallography

Data collection

The data were recorded at $(15 \pm 1)^\circ\text{C}$ to a maximum 2θ of 55.0° . Data collection and processing parameters are summarized in Table 2. The structure was solved by direct methods¹⁴ and expanded by using Fourier techniques.¹⁵ The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3084 observed reflections [$I > 3.00\sigma(I)$] and 398 variable parameters. Neutral atom scattering factors and anomalous dispersion effects were taken from Cromer¹⁶ and Ibers,¹⁷ respectively.

Table 2 Data collection and processing parameters for CdL^1

Empirical formula	$\text{C}_{30}\text{H}_{40}\text{N}_8\text{Cl}_4\text{Cd}_2$
Formula weight	879.34
a (nm)	2.6016(7)
b (nm)	0.9673(2)
c (nm)	1.4964(7)
β ($^\circ$)	114.364(4)
Volume (nm^3)	3.4303
Z	4
Space group	C_c (# 9)
μ (Mo $K\alpha$) (cm^{-1})	15.87
Crystal size (mm)	$0.50 \times 0.20 \times 0.10$
Crystal system	monoclinic
Lattice type	C -centered
Unique data	3497
Observed data	3084
$F(000)$	1760.00
R	0.029
wR	0.041
W	$[\sigma^2(F) + 0.0007]^{-1}$

Description of the structure of CdL^1

The molecular structure is shown in Fig. 1. There are two coordinate centers outside of the macrocycle ring in the dinuclear complex, and consequently the environments of the two cadmium cations are identical. Each cadmium atom is five coordinated by three N atoms and two chlorine atoms. The cadmium center is in a distorted trigonal bipyramidal environment. The atomic coordinates are listed in Table 3, and selected bond lengths and angles in Tables 4 and 5, respectively. Two five-membered

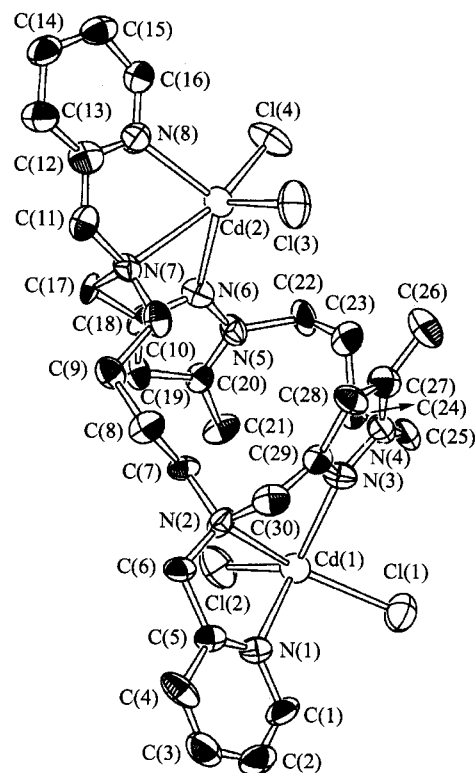


Fig. 1 Molecular structure of CdL^1 .

chelate rings are present in each coordinate center of cadmium, one is through bonding to the tertiary amine nitrogen atom N(2) and the pyrazolyl nitrogen atom N(3); another is through bonding to N(2) and the pyridyl nitrogen atom N(1). The dihedral angle of the two planes is about 48.0° . The bond lengths of Cd—N(1) and Cd—N(3) are about 0.23 nm whereas the bond length of Cd—N(2) is 0.252 nm, indicating that the aromatic nitrogen atoms are much stronger donor atoms to Cd than the tertiary amine N atoms. The Cd—Cl bond lengths in the complex are from 0.242 to 0.249 nm which could be regarded that the Cd—Cl bonds are present as polar covalent bonds. The Cl(1)-Cd-N(2) bond angle (153.5°) is the largest at Cd and could be regarded as the axis of the distorted trigonal bipyramid. The three angles at Cd in the "trigonal plane" formed by N(1), N(3) and Cl(2) are in the range of 103.1° — 123.5° . However, N(1)-Cd-N(2) and N(2)-Cd-N(3) are significantly near 70° , with distortion of the trigonal bipyramid by displacement of Cd towards Cl. The dihedral angle between the two pyrazolyl ring planes is 32.3° , which means that the macrocycle ring can be distorted easily for satisfying the need of coordination of N(3) to Cd with the aid of the two soft $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ fragments in the macrocycle.

Table 3 Atomic coordinates and B_{eq}

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cd(1)	0.67283(2)	-0.20810(4)	0.95528(4)	3.103(8)
Cd(2)	0.38753(2)	-0.20726(4)	0.48385(4)	3.149(9)
Cl(1)	0.72907(8)	-0.4242(2)	1.0100(1)	4.69(3)
Cl(2)	0.60298(9)	-0.2061(2)	1.0271(2)	5.07(4)
Cl(3)	0.45714(9)	-0.2074(2)	0.4154(2)	5.35(4)
Cl(4)	0.33225(9)	-0.4205(2)	0.4286(1)	5.12(4)
N(1)	0.7377(2)	-0.0380(5)	1.0460(3)	3.08(8)
N(2)	0.4682(2)	0.0203(5)	0.8653(4)	2.99(7)
N(3)	0.6472(2)	-0.2462(5)	0.7905(4)	2.88(7)
N(4)	0.6262(2)	-0.3471(5)	0.7231(4)	3.02(8)
N(5)	0.4348(2)	-0.3439(4)	0.7159(4)	2.92(8)
N(6)	0.4133(2)	-0.2370(5)	0.6505(3)	2.84(7)
N(7)	0.4123(2)	0.0193(5)	0.5756(3)	2.72(6)
N(8)	0.3244(2)	-0.0432(5)	0.4009(4)	3.41(8)
C(1)	0.7854(3)	-0.0803(8)	1.1285(4)	4.1(1)
C(2)	0.8216(3)	0.0185(9)	1.1846(6)	4.6(1)
C(3)	0.8085(3)	0.1557(9)	1.16443(6)	5.2(1)
C(4)	0.7649(3)	0.1987(6)	1.0809(5)	4.1(1)
C(5)	0.7287(2)	0.0896(6)	1.0199(4)	2.74(8)
C(6)	0.6730(3)	0.1329(6)	0.9280(4)	3.13(9)
C(7)	0.5863(2)	0.0331(6)	0.8150(4)	2.67(8)
C(8)	0.5639(3)	0.1487(5)	0.7415(5)	4.0(1)
C(9)	0.4990(2)	0.1497(6)	0.6948(4)	3.31(9)
C(10)	0.4747(3)	0.0330(5)	0.6181(5)	3.23(9)
C(11)	0.3819(2)	0.1334(5)	0.5041(5)	3.23(9)
C(12)	0.3333(3)	0.0950(6)	0.4209(5)	3.59(10)
C(13)	0.2971(3)	0.1906(6)	0.3643(5)	3.9(1)
C(14)	0.2518(3)	0.1576(8)	0.2754(5)	4.3(1)
C(15)	0.2470(2)	0.0203(8)	0.2498(4)	3.86(10)
C(16)	0.2824(3)	-0.0715(7)	0.3179(5)	3.8(1)
C(17)	0.3869(2)	0.0051(4)	0.6483(3)	2.07(7)
C(18)	0.4088(2)	-0.1313(5)	0.7026(4)	2.67(8)
C(19)	0.4289(2)	-0.1600(5)	0.7949(4)	2.87(8)
C(20)	0.4431(3)	-0.3078(5)	0.8044(4)	2.80(8)
C(21)	0.4654(3)	-0.3992(6)	0.8974(5)	3.8(1)
C(22)	0.4508(3)	-0.4769(5)	0.6845(5)	3.8(1)
C(23)	0.5038(3)	-0.4710(6)	0.6720(5)	3.49(9)
C(24)	0.5562(2)	-0.4591(5)	0.7700(4)	3.02(8)
C(25)	0.6137(2)	-0.4746(5)	0.7589(4)	3.18(9)
C(26)	0.5950(3)	-0.3842(7)	0.5458(5)	4.7(1)
C(27)	0.6166(3)	-0.2956(6)	0.6290(5)	3.57(10)
C(28)	0.6347(3)	-0.1718(7)	0.6366(4)	3.47(9)
C(29)	0.6518(2)	-0.1334(6)	0.7416(4)	2.83(8)
C(30)	0.6720(3)	-0.0078(6)	0.7954(4)	3.57(10)

Table 4 Selected bond lengths (nm)

Atom	Distance	Atom	Distance
Cd(1)—Cl(1)	0.2489(2)	Cd(1)—Cl(2)	0.2463(3)
Cd(1)—N(1)	0.2347(5)	Cd(1)—N(2)	0.2528(5)
Cd(1)—N(3)	0.2303(5)	Cd(2)—Cl(3)	0.2421(3)
Cd(2)—Cl(4)	0.2455(2)	Cd(2)—N(6)	0.2318(5)
Cd(2)—N(7)	0.2524(4)	Cd(2)—N(8)	0.2252(5)
N(1)—C(1)	0.1402(7)	N(1)—C(5)	0.1286(7)
N(2)—C(6)	0.1409(7)	N(2)—C(7)	0.1474(6)
N(2)—C(30)	0.1444(10)	N(3)—N(4)	0.1347(7)
N(3)—C(29)	0.1346(8)	N(4)—C(25)	0.1436(8)
N(4)—C(27)	0.1414(9)	N(5)—N(6)	0.1374(6)
N(5)—C(20)	0.1298(8)	N(5)—C(22)	0.1488(8)
N(6)—C(18)	0.1319(7)	N(7)—C(10)	0.1485(8)
N(7)—C(11)	0.1513(7)	N(7)—C(17)	0.1495(8)
N(8)—C(12)	0.1369(8)	N(8)—C(16)	0.1301(7)

Table 5 Selected bond angles (°)

Atom	Angle
Cl(1)—Cd(1)—Cl(1)	107.60(7)
Cl(1)—Cd(1)—N(1)	102.3(1)
Cl(1)—Cd(1)—N(2)	153.5(1)
Cl(1)—Cd(1)—N(3)	95.1(1)
Cl(2)—Cd(1)—N(1)	103.1(2)
Cl(2)—Cd(1)—N(2)	98.9(1)
Cl(2)—Cd(1)—N(3)	121.9(1)
N(1)—Cd(1)—N(2)	70.1(1)
N(1)—Cd(1)—N(3)	123.5(2)
N(2)—Cd(1)—N(3)	70.9(2)
Cl(3)—Cd(2)—Cl(4)	107.07(8)
Cl(3)—Cd(2)—N(6)	121.4(1)
Cl(3)—Cd(2)—N(7)	99.4(1)
Cl(3)—Cd(2)—N(8)	105.6(2)
Cl(4)—Cd(2)—N(6)	97.3(1)
Cl(4)—Cd(2)—N(7)	153.6(1)
Cl(4)—Cd(2)—N(8)	102.4(1)
N(6)—Cd(2)—N(7)	68.1(1)
N(6)—Cd(2)—N(8)	120.1(2)
N(7)—Cd(2)—N(8)	69.7(2)
Cd(1)—N(1)—C(1)	117.9(4)
Cd(1)—N(1)—C(5)	119.9(3)
Cd(1)—N(2)—C(6)	112.1(3)
Cd(1)—N(2)—C(7)	109.2(3)
Cd(1)—N(2)—C(30)	97.5(3)
Cd(1)—N(3)—N(4)	140.1(4)
Cd(1)—N(3)—C(29)	113.6(3)
Cd(2)—N(6)—N(5)	135.4(4)
Cd(2)—N(6)—C(18)	118.9(3)
Cd(2)—N(7)—C(10)	107.4(3)
Cd(2)—N(7)—C(11)	107.9(3)
Cd(2)—N(7)—C(17)	103.1(3)
Cd(2)—N(8)—C(12)	123.3(4)
Cd(2)—N(8)—C(16)	120.8(4)

Experimental

Methods and materials

Melting points were determined on a WC-1 microscopic apparatus and were uncorrected. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer. ^1H NMR spectra were recorded on a Bruker DPX400 spectrometer using TMS as internal standard. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer. UV-visible spectra were recorded on a Shimadzu 2100 spectrophotometer. Mass spectra were obtained on a JMSD 100 spectrometer by the impact method.

All solvents used in the syntheses were of analytical grade. Transition metal chlorides were commercially available. Metal picrates were prepared according to the literature method.¹⁸ *N, N'*-Bis(2-pyridylmethyl)-1,4-diaminobutane and *N, N'*-bis(*o*-methoxybenzyl)-1,4-diaminobutane were prepared following mainly the procedure of Goodwin¹⁹ and Billman,²⁰ respectively. 5-Methyl-3-methoxycarbonyl pyrazole was prepared by the method of Ramdani.²¹

Syntheses of ligands

1,4-Bis(3'-methoxycarbonyl-5'-methyl-1'-pyrazolyl)butane (1)

A mixture of 3-methoxycarbonyl-5-methyl pyrazole (22.4 g, 0.16 mol), 1,4-dibromobutane (17.3 g, 0.08 mol) and *t*-BuOK (20 g, 0.176 mol) in anhydrous THF (60 mL) was refluxed for 10 h and then filtered. The filtrate was evaporated to dryness. The residue obtained was purified by chromatography on an alumina column (eluent: $\text{CHCl}_3/\text{C}_2\text{H}_5\text{OH}$, 9/1, *V/V*), and 2.3 g of **1** was obtained as colorless oil, yield 86%. ^1H NMR (CDCl_3) δ : 2.25 (s, 6H, CH_3Pz , $\text{Pz} = \text{Pyrazole}$), 2.39—2.43 (m, 4H, $\text{CCH}_2\text{CH}_2\text{C}$), 4.13 (t, $J = 3.5$ Hz, 4H, CH_2Pz), 3.95 (s, 6H, OCH_3), 6.55 (s, 2H, H-Pz). Anal. calcd for $\text{C}_{16}\text{H}_{22}\text{N}_4\text{O}_4$: C 57.47, H 6.63, N 16.76; found C 57.65, H 6.48, N 16.84.

1,4-Bis(3'-chloromethyl-5'-methyl-1'-pyrazolyl)butane (2)

A solution of 2.0 g (6.0 mmol) of **1** in anhydrous THF (50 mL) was slowly added to a suspension of LiAlH_4

(2.0 g) in anhydrous THF (150 mL). The mixture was refluxed for 4 h. After cooling to room temperature, 2 mL of H_2O and 5 mL of aqueous NaOH (0.3 g of NaOH in 5 mL of H_2O) were slowly added successively and then refluxed for 1 h. After washed with 3×50 mL of water, the organic phase was dried over anhydrous MgSO_4 and evaporated to dryness to give a white solid, yield 92%. ^1H NMR (CDCl_3) δ : 2.13 (s, 6H, CH_3Pz), 2.10—2.30 (m, 4H, $\text{CCH}_2\text{CH}_2\text{C}$), 3.95 (t, $J = 3.0$ Hz, 4H, CH_2Pz), 4.40 (s, 4H, CH_2O), 6.02 (s, 2H, H-Pz).

A solution of the diol in SOCl_2 (20 mL) was stirred at room temperature overnight. The solvent was distilled to dryness under reduced pressure. The residue was suspended in CH_2Cl_2 (30 mL) and neutralized with aqueous Na_2CO_3 solution. After drying on anhydrous Na_2SO_4 , the organic phase was evaporated to dryness to give 1.65 g (94% yield) of **2** as white solid which should be used immediately. ^1H NMR (CDCl_3) δ : 2.12 (s, 6H, CH_3Pz), 2.25—2.40 (m, 4H, $\text{CCH}_2\text{CH}_2\text{C}$), 3.92 (t, $J = 2.5$ Hz, 4H, CH_2Pz), 4.55 (s, 4H, CH_2Cl), 6.12 (s, 2H, H-Pz). Anal. calcd for $\text{C}_{14}\text{H}_{20}\text{N}_4\text{Cl}_2$: C 53.34, H 6.35, N 17.78; found C 53.26, H 6.54, N 17.69.

Syntheses of macrocycle L^1 and L^2

General method

Solutions of **2** (0.01 mol) in CH_3CN (100 mL) and the corresponding diamino-compound (0.01 mol) in 100 mL of CH_3CN were simultaneously added to a refluxed suspension of Na_2CO_3 (0.05 mol) in 300 mL of CH_3CN in about 2 h. The mixture was vigorously stirred and refluxed for 20 h and then filtered on celite. The residue obtained after evaporation of solvent was purified by chromatography on a silica column (eluent: $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 9/1, *V/V*) to give the corresponding product.

L^1 Yield 45%, m. p. 119—120 °C; UV-vis (CH_3OH) λ_{max} : 223.0, 261.0 nm; ^1H NMR (CDCl_3) δ : 7.05—8.66 (m, 8H, H-Py), 5.98 (s, 2H, H-Pz), 4.02 (t, $J = 7$ Hz, 4H, $\text{PzCH}_2\text{CCCH}_2\text{Pz}$), 3.85 (s, 4H, $\text{PzCH}_2\text{Nsp}^3$), 3.54 (s, 4H, $\text{PyCH}_2\text{Nsp}^3$), 2.36 (t, $J = 7$ Hz, 4H, $\text{Nsp}^3\text{CH}_2\text{CCCH}_2\text{Nsp}^3$), 2.27 (s, 6H, CH_3Pz), 1.65—1.72 (m, 4H, $\text{PzCCH}_2\text{CH}_2\text{CPz}$), 1.30—1.35 (m, 4H, $\text{Nsp}^3\text{CCH}_2\text{CH}_2\text{CNsp}^3$); IR (KBr) ν : 2900, 2855, 1588, 1546, 1475, 1430,

1315, 1255, 1140, 1070, 1048, 760 cm^{-1} ; MS m/z : 512 (M^+). Anal. calcd for $\text{C}_{30}\text{H}_{40}\text{N}_8$: C 70.31, H 7.81, N 21.86; found C 70.56, H 7.78, N 21.68.

L² Oil, yield 50%; UV-vis (CH_3OH) λ_{max} : 223.5, 274.0 nm; ^1H NMR (CDCl_3) δ : 7.60—6.80 (m, 8H, H-Ar), 5.95 (s, 2H, H-Pz), 3.91 (t, $J = 3$ Hz, 4H, $\text{PzCH}_2\text{CCCH}_2\text{Pz}$), 3.84 (s, 4H, $\text{PzCH}_2\text{Nsp}^3$), 3.75 (s, 6H, CH_3O), 3.65 (s, 4H, $\text{ArCH}_2\text{Nsp}^3$), 2.34 (t, $J = 3.5$ Hz, 4H, $\text{Nsp}^3\text{CH}_2\text{CCCH}_2\text{Nsp}^3$), 2.23 (s, 6H, CH_3Pz), 1.70—1.80 (m, 4H, $\text{PzCCH}_2\text{CH}_2\text{CPz}$), 1.30—1.35 (m, 4H, $\text{Nsp}^3\text{CCH}_2\text{CH}_2\text{CNsp}^3$); IR (KBr) ν : 2900, 2850, 1590, 1530, 1460, 1380, 1350, 1280, 1236, 746 cm^{-1} ; MS m/z : 570 (M^+). Anal. calcd for $\text{C}_{34}\text{H}_{46}\text{N}_6\text{O}_2$: C 71.58, H 8.07, N 14.74; found C 71.64, H 8.15, N 14.65.

Preparation of complexes

Potassium picrate complexes of macrocycle **L¹** (**KL¹**) and **L²** (**KL²**)

To a solution of potassium picrate (0.5 mmol) in ethanol (20 mL) was added dropwise a solution of **L** (0.5 mmol in 5 mL of ethanol). The resulting yellow mixture was refluxed for 5 h and then cooled slowly to room temperature. The yellow complex precipitating out from the solution was collected and washed with cooled ethanol and diethyl ether and dried in vacuum to give the corresponding complex.

KL¹ Yield 89%, m. p. 75—77 °C; UV-vis (CH_3OH) λ_{max} : 217.0, 260.2, 353.0 nm; ^1H NMR ($\text{DMSO}-d_6$) δ : 8.58 (s, 2H, H-Pic), 8.47—7.23 (m, 8H, H-Py), 5.93 (s, 2H, H-Pz), 3.96 (t, $J = 2.5$ Hz, 4H, $\text{PzCH}_2\text{CCCH}_2\text{Pz}$), 3.74 (s, 4H, PzCH_2N), 3.44 (s, 4H, CH_2Py), 2.26 (s, 6H, CH_3Pz), 2.20 (t, $J = 2.8$ Hz, 4H, $\text{Nsp}^3\text{CH}_2\text{CCCH}_2\text{Nsp}^3$), 1.65—1.75 (br, 4H, $\text{PzCCH}_2\text{CH}_2\text{CPz}$), 1.24—1.30 (br, 4H, $\text{Nsp}^3\text{CCH}_2\text{CH}_2\text{CNsp}^3$); IR (KBr) ν : 1625, 1545, 1440, 1360, 1260, 1145, 758 cm^{-1} . Anal. calcd for $\text{C}_{36}\text{H}_{44}\text{N}_{11}\text{O}_8\text{K}$ (**L¹**·**KPic**· H_2O): C 54.19, H 5.52, N 19.32; found C 54.48, H 5.76, N 19.62.

KL² Yield 85%, m. p. 69—72 °C; UV-vis (CH_3OH) λ_{max} : 219.0, 271.5, 353.0 nm; ^1H NMR ($\text{DMSO}-d_6$) δ : 8.56 (s, 2H, H-Pic), 7.35—6.90 (m, 8H, H-Ar), 5.98 (s, 2H, H-Pz), 3.95 (t, $J = 2.5$ Hz, 4H, $\text{PzCH}_2\text{CCCH}_2\text{Pz}$), 3.85 (s, 4H, $\text{PzCH}_2\text{Nsp}^3$), 3.75 (s, 6H, CH_3O), 3.62 (s, 4H, $\text{ArCH}_2\text{Nsp}^3$), 2.29 (t, $J = 1.8$ Hz, 4H, $\text{Nsp}^3\text{CH}_2\text{CCCH}_2\text{Nsp}^3$), 2.25 (s, 6H, CH_3Pz), 1.70—1.80 (m, 4H, $\text{PzCH}_2\text{CCCH}_2\text{Pz}$), 1.36—1.42 (br, 4H, $\text{Nsp}^3\text{CCH}_2\text{CH}_2\text{CNsp}^3$); IR (KBr) ν : 1625, 1605, 1550, 1480, 1430, 1335, 1260, 755 cm^{-1} . Anal. calcd for $\text{C}_{40}\text{H}_{50}\text{N}_9\text{O}_{10}\text{K}$ (**L²**·**KPic**· H_2O): C 56.14, H 5.85, N 14.74; found C 56.25, H 5.69, N 14.77.

Cobalt complexes of macrocycle **L¹** (**CoL¹**) and **L²** (**CoL²**)

A mixture of cobalt chloride (hydrate, 0.3 mmol) and **L** (0.3 mmol) in methanol (50 mL) was stirred and refluxed for 24 h. Filtered at hot and cooled slowly to room temperature. The precipitate obtained after standing was collected and washed with cooled methanol and dried.

CoL¹ Yield 90%, m. p. 133—135 °C; UV-vis (CH_3OH) λ_{max} : 215.8, 264.0 nm; IR (KBr) ν : 3505, 1595, 1543, 1445, 1390, 1115, 765 cm^{-1} . Anal. calcd for $\text{C}_{30}\text{H}_{42}\text{Cl}_2\text{N}_8\text{OCo}$ (**L¹**·**CoCl₂**· H_2O): C 54.55, H 6.36, N 16.97; found C 54.18, H 6.56, N 16.54.

CoL² Yield 78%, m. p. 165—168 °C; UV-vis (CH_3OH) λ_{max} : 226.0, 275.0 nm; IR (KBr) ν : 3500, 1595, 1540, 1455, 1388, 1385, 1240, 1125, 1020, 750 cm^{-1} . Anal. calcd for $\text{C}_{68}\text{H}_{94}\text{Cl}_6\text{N}_{12}\text{O}_5\text{Co}_3$ (**2L²**·**3CoCl₂**· H_2O): C 52.71, H 6.07, N 10.85; found C 52.88, H 5.95, N 11.23.

Cadmium complexes of macrocycle **L¹** (**CdL¹**) and **L²** (**CdL²**)

CdL¹ and **CdL²** were prepared by the same method as that for the cobalt complexes.

CdL¹ Yield 84%, m. p. 249—250 °C; UV-vis (CH_3OH) λ_{max} : 225.0, 264.5 nm; ^1H NMR ($\text{DMSO}-d_6$) δ : 8.64, 7.52—8.06 (m, 8H, H-Py), 6.04 (s, 2H, H-Pz), 4.39 (t, $J = 2.0$, 4H, $\text{PzCH}_2\text{CCCH}_2\text{Pz}$), 3.96 (s, 4H, $\text{PzCH}_2\text{Nsp}^3$), 3.84 (s, 4H, CH_2Py), 2.30—2.60 (m, 10H, CH_3Pz , $\text{Nsp}^3\text{CH}_2\text{CCH}_2\text{Nsp}^3$), 1.70—1.84 (m, 4H, $\text{PzCCH}_2\text{CH}_2\text{CPz}$), 1.21—1.30 (m, 4H, $\text{Nsp}^3\text{CCH}_2\text{CH}_2\text{CNsp}^3$); IR (KBr) ν : 1600, 1542, 1480, 1440, 1390, 1296, 1105, 760 cm^{-1} . Anal. calcd for $\text{C}_{30}\text{H}_{40}\text{Cl}_4\text{N}_8\text{Cd}_2$ (**L¹**·**CdCl₂**): C

41.00, H 4.56, N 12.76; found C 40.89, H 4.57, N 12.69.

CdL² Yield 80%, m.p. 158—160 °C; UV-vis (CH₃OH) λ_{\max} : 228.0, 276.5 nm; ¹H NMR (DM-SO-*d*₆) δ : 6.85—7.62 (m, 8H, H-Ar), 6.02 (s, 2H, H-Pz), 3.98 (t, *J* = 2.0, 4H, PzCH₂CCCH₂Pz), 3.89 (s, 4H, PzCH₂Nsp³), 3.76 (s, 6H, CH₃O), 3.69 (s, 4H, ArCH₂Nsp³), 2.36 (t, *J* = 1.9, 4H, Nsp³CH₂CCCH₂Nsp³), 2.32 (s, 6H, CH₃Pz), 1.70—1.80 (m, 4H, PzCCH₂CH₂CPz), 1.30—1.38 (m, 4H, Nsp³CCH₂CH₂CNsp³); IR (KBr) ν : 2900, 2855, 1598, 1550, 1480, 1450, 1280, 1240, 1050, 750 cm⁻¹. Anal. calcd for C₃₄H₄₈Cl₂N₆O₃Cd (L²·CdCl₂·H₂O): C 52.92, H 6.23, N 10.89; found C 52.89, H 6.37, N 10.56.

Transport of metal cations across a liquid membrane

The apparatus described by Ramdani²¹ was used (*a* = 10 mm, *b* = 35 mm, *c* = 54 mm). Source phase: aqueous solution (15 mL) of picrate (1 × 10⁻³ mol/L) and nitrate (0.1 mol/L). Membrane: CH₂Cl₂ solution (45 mL) of the ligand to be studied (5 × 10⁻³ mol/L). Receiving phase: distilled water (15 mL). The transport experiments were performed at (25 ± 1) °C. The appearance of picrate anion in the receiving phase was detected by UV spectroscopy at 355 nm.

X-Ray structure determination

Crystals of CdL² were grown from methanol solution at room temperature. A white acicular crystal of dimension 0.5 mm × 0.2 mm × 0.1 mm were mounted on a glass fiber. All measurements were made on a RAXIS-IV imaging plate area detector with graphite monochromated Mo K α radiation. Determination of the crystal class, orientation matrix and accurate uni-cell parameters was performed according to the established procedures.²²

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