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Synthesis, stability and structural characterization of a new macrocyclic ligand with four neutral pendent groups: 1,4,7,10-tetrakisbenzyl-1,4,7,10-tetraazacyclo dodecane (L) and its Co and Cu complexes

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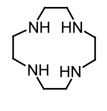
Abstract

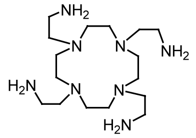
Two new divalent metal complexes of general formula: $M(NO_3)_2(L)nH_2O$ [M = Co (**1**), $n = 0$; M = Cu (**2**), $n = 2$] which coordinated to a new macrocyclic ligand, 1,4,7,10-tetrakisbenzyl-1,4,7,10-tetraazacyclododecane (L) have been synthesized and characterized structurally by X-ray diffraction. In complex **1**, the central Co atom coordinately bonds to four nitrogen atoms of the macrocyclic ligand and two oxygen atoms of a nitrate anion, to form a slightly distorted octahedron. X-ray diffraction indicated that the bonds lengths of Co–N(1) and Co–N(2) are 2.212(7), 2.230(7) Å, respectively. Bond lengths between Co and two oxygen atoms are the same: Co–O(1) 2.142(7) Å. In complex **2** four nitrogen atoms of macrocyclic ligand coordinated to copper atom together with an oxygen atom from water molecule, which defined a five-coordinated tetragonal pyramid. The distances between Cu and nitrogen atoms are Cu–N(1) 2.020(7) Å and Cu–N(2) 2.030(6) Å, respectively. The bond length of Cu–O(1) is 2.126(6) Å. Potentiometric measurements were determined in 1,4-dioxane–water for L, Co and Cu complexes with the formation constants: $\log K[ML] = 19.79$ for Co and 15.61 for Cu.

Keywords: Cobalt; Copper; Tetraazamacrocyclic Ligand; Stability constants; X-ray structures

1. Introduction

The successful application of several 1,4,7,10-tetraazacyclododecane (Cyclen) precursors in the synthesis of macrocyclic complexes stems mainly from their use as models for protein–metal binding sites in biological systems [1], and as selective complexing agents for metal ions [2–4], such as therapeutic reagents for the treatment of metal toxicity [5,6]. Nowadays interest is focused on the synthesis of macrocyclic complexes with potential medicinal applications, as contrast-enhancing agents in magnetic resonance imaging (MRI) [7,8], as NMR shift and relaxation reagents [9,10], and as RNA cleavage catalysts [11,12]. These potential and versatile applications have stimulated research in the synthesis of novel Cyclen-based ligands with varying types and numbers of pendent arms in an attempt to find new ligands having different chemical, biological or catalytic properties.


Cyclen(L")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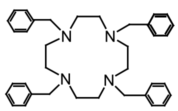
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In this paper we describe the synthesis of macrocyclic cobalt(II), copper(II) complexes with a new type of Cyclen-based ligand having four neutral pendent groups at N residuals, which have shown high anti-tumor activities in an MTT assay to HL-60 tumor cell lines in our former reports [13]. Structures of Co and Cu

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complexes are determined by X-ray diffraction. Also the thermodynamic stability of these two complexes are studied via potentiometric methods.

2. Experimental

2.1. Materials and methods

The ligand was synthesized as reported previously [13]. GR grade 1,4-dioxane, H_2SO_4, HBr, MeOH, NaOH and KCl were purchased from EM Sciences Industries Inc. $Co(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ were obtained from Aldrich. IR spectra were recorded on a Perking Elmer 983G spectrometer in the range of 4000–400 cm^{-1} using KBr pellets. UV–Vis spectra were recorded on a Shimadazu UV-240 spectrometer. Elemental analysis was performed on a P-E 240C analyzer. All of the metal stock solutions for the potentiometric studies were reagent grade nitrate salt solutions prepared with doubly distilled water and standardized with ion exchange resin. CO_2-free Dilute-it ampoules of KOH were obtained from J.T. Baker Inc. KOH solutions (about 0.1 M) were prepared with doubly distilled water and standardized against potassium biphthalate with phenolphthalein as an indicator. The extent of carbonate accumulation was checked periodically by titration with a standard HCl solution.

2.2. Potentiometric equipment

A Corning 250 digital p[H] meter, fitted with Fisher full-range blue-glass and Fisher calomel reference electrodes, was used for potentiometric titrations. A Metrohm 10-ml capacity piston buret was used for precise delivery of the standard KOH. The solution to be studied was contained in a 75-ml jacketed glass cell thermostated at 25 ± 0.05 °C by a circulating constant-temperature water bath.

2.3. Potentiometric determinations

All p[H] calibrations were performed with standardized HCl aqueous solutions to measure hydrogen ion concentrations directly ($p[H] = -\log[H]^+$). The ionic strength was adjusted to 0.100 M with KCl. The electrodes were calibrated by taking the average calculated E° of 20 separate titration points of a titration of dilute standardized HCl. Titrations of the ligand in the absence or presence of metal ions in aqueous solution were conducted in the manner described by Martell and Motekaitis [14]. Cell solutions (generally, 50 ml) were purged with a purified argon stream to create an inert atmosphere. Standard base was introduced into the sample solutions with a Metrohm piston buret in small increments. Adding increments of standard base to a solution containing ligand plus other components (KCl solution, metal solution) carried out experimental runs. The p[H] range for accurate measurements was considered to be 2–12. The pK_w for the mixed aqueous system, defined as $-\log([H^+][OH^-])$ at the ionic strength employed, was found to be 16.00 for 1,4-dioxane–water (70:30 v/v).

2.4. Computations

Protonation constants and stability constants from the direct titrations were calculated from the potentiometric data with the program BEST developed by Martell group. The error in the constants listed in Table 1 is estimated as ± 0.02 log unit on the basis of the σ_{fit} value, which measures the deviation of the experimental curve and the curve calculated from the equilibrium constants, being less than 0.01 p[H] unit in all potentiometric determinations. Species distribution diagrams were computed from the measured equilibrium constants with SPE and plotted with SPEPLOT.

2.5. Synthesis of the cobalt and copper complexes

2.5.1. $Co(C_{36}H_{44}N_4)(NO_3)_2$

To a suspension of L (226 mg,0.5 mmol) in EtOH (15 ml), $Co(NO_3)_2\cdot 6H_2O$ (145 mg, 0.5 mmol) was added at 50 °C. The solution changed from pink to violet. The reaction mixture was stirred overnight, then filtered, and

Table 1
Crystallographic data for the cobalt and copper complexes

Molecular formula	$C_{36}H_{44}N_6O_6Co$	$C_{36}H_{48}N_6O_8Cu$
Formula weight	715.71	756.34
Crystal color; habit	red, prismatic	blue, prismatic
Crystal dimensions (mm^3)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
Crystal system	orthorhombic	monoclinic
Unit cell dimensions		
a (Å)	24.146(7)	9.542(2)
b (Å)	8.080(5)	16.757(3)
c (Å)	17.860(6)	11.323(2)
β (°)		102.20(3)
V ($Å^3$)	3484(5)	1769.6(6)
Space group	$Cmc2_1$	$P2_1/m$
Z	4	2
D_{calc} (g cm^{-3})	1.364	1.419
$F(000)$	1508.00	798
θ_{max} (°)	25	27
μ (cm^{-1})	5.47	0.678
Function minimized	$\Sigma\ \varpi(\lvert F_o\rvert-\lvert F_c\rvert)^2$	$\Sigma\ \varpi(\lvert F_o\rvert-\lvert F_c\rvert)^2$
p-factor	0.03	0.03
No. observations ($I > 2.5\sigma(I)$ and $I > 2\sigma(I)$)	1544	1316
No. variables	231	247
Residuals: R, R_w	0.074, 0.090	0.087, 0.1442
Goodness-of-fit	3.65	1.103
Maximum shift of final cycle	0.01	0.00
Peak, hole in final difference map (e $Å^{-3}$)	0.47; −0.48	0.49; −0.45

Table 2
Selected bond lengths (Å) and bond angles (°) of $[(C_{36}H_{44}N_4)Co(NO_3)](NO_3)$

Bond lengths			
Co–O(1)	2.142(7)	C(1)–C(2)	1.52(1)
Co–N(1)	2.212(7)	C(2)–C(3)	1.38(1)
Co–N(2)	2.230(7)	C(2)–C(7)	1.39(1)
O(1)–N(3)	1.273(9)	C(3)–C(4)	1.38(1)
O(2)–N(3)	1.21(1)	C(4)–C(5)	1.38(2)
O(3)–N(4)	1.24(2)	C(5)–C(6)	1.35(2)
O(4)–N(4)	1.25(1)	C(6)–C(7)	1.41(1)
O(5)–N(4)	1.22(2)	C(8)–C(9)	1.25(2)
N(1)–C(1)	1.50(1)	C(10)–C(11)	1.52(1)
N(1)–C(8)	1.49(2)	C(11)–C(12)	1.38(1)
N(1)–C(17)	1.50(2)	C(11)–C(16)	1.31(2)
N(2)–C(9)	1.46(1)	C(12)–C(13)	1.34(2)
N(2)–C(10)	1.52(1)	C(13)–C(14)	1.36(2)
N(2)–C(18)	1.43(2)	C(15)–C(16)	1.44(2)
C(14)–C(15)	1.36(2)	C(17)–C(17)	1.14(4)
C(18)–C(18)	1.31(3)		
Bond angles			
O(1)–Co–O(1)	60.0(4)	C(9)–N(2)–C(18)	109.0(1)
O(1)–Co–N(1)	91.2(3)	C(10)–N(2)–C(18)	113.0(1)
O(1)–Co–N(1)	132.6(3)	N(1)–C(1)–C(2)	114.5(7)
O(1)–Co–N(2)	92.7(2)	C(1)–C(2)–C(3)	120.2(8)
O(1)–Co–N(2)	133.0(3)	C(1)–C(2)–C(7)	121.3(8)
O(1)–Co–N(1)	132.6(3)	C(3)–C(2)–C(7)	118.4(8)
N(1)–Co–N(1)	82.2(5)	C(2)–C(3)–C(4)	121.0(1)
N(1)–Co–N(2)	80.0(3)	C(3)–C(4)–C(5)	120.0(1)
N(1)–Co–N(2)	131.4(3)	C(4)–C(5)–C(6)	121.0(1)
N(2)–Co–N(2)	78.9(4)	C(5)–C(6)–C(7)	119.0(1)
Co–O(1)–N(3)	92.8(6)	C(2)–C(7)–C(6)	121.0(1)
Co–N(1)–C(1)	113.5(5)	N(1)–C(8)–C(9)	124.0(1)
Co–N(1)–C(8)	105.7(7)	N(2)–C(9)–C(8)	122.0(1)
Co–N(1)–C(17)	102.6(7)	C(1)–N(1)–C(17)	108.8(9)
Co–N(2)–C(9)	106.7(7)	C(10)–C(11)–C(12)	119.2(9)
Co–N(2)–C(10)	110.9(5)	C(10)–C(11)–C(16)	122.0(1)
Co–N(2)–C(18)	107.8(6)	C(12)–C(13)–C(14)	118.0(1)
C(1)–N(1)–C(8)	110.0(1)	C(13)–C(14)–C(15)	123.0(1)
N(2)–C(10)–C(11)	116.5(7)	N(1)–C(17)–C(17)	126.3(6)
C(8)–N(1)–C(17)	116.0(2)	N(2)–C(18)–C(18)	122.2(6)
C(12)–C(11)–C(16)	119.0(1)	C(9)–N(2)–C(10)	109.6(9)
C(11)–C(12)–C(13)	122.0(1)	C(14)–C(15)–C(16)	117.0(1)
C(11)–C(16)–C(15)	120.0(1)		

the red residue was washed repeatedly with CH_2Cl_2 and EtOH. The product was dried over P_2O_5 in vacuo. Yield: 220 mg, 61%. M.p. (dec.) 215 °C. *Anal.* Found: C, 60.21; H, 6.30; N, 11.38. Calc. for $Co(C_{36}H_{44}N_4)(NO_3)_2$: C, 60.41; H, 6.20; N, 11.74%. IR spectrum (KBr pellet): 2841w, 1475m, 1385s, 1335s, 1065m, 950w, 706m cm^{-1}.

2.5.2. $Cu(C_{36}H_{44}N_4)(NO_3)_2 \cdot 1.5H_2O$

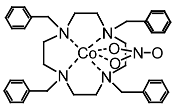
$Cu(NO_3)_2 \cdot 6H_2O$ (121 mg, 0.5 mmol) was dissolved into EtOH (20 ml) at 60 °C with stirring. Then L (226 mg, 0.5 mmol) was added to this solution, meanwhile a blue precipitate deposited quickly. The reaction mixture slurry was stirred overnight. After filtration using a sintered glass filter, dark blue crystals were obtained which were washed twice with 1:1 Et_2O:EtOH. The product was dried over $CaCl_2$. Yield: 344 mg, 92%. M.p. (dec.) 185 °C. *Anal.* Found: C, 57.91; H, 6.67; N, 11.78. Calc. for $Cu(C_{36}H_{44}N_4)(NO_3)_2 \cdot 1.5H_2O$: C, 57.85; H, 6.34; N, 11.24%. IR spectrum (KBr pellet): 3425b,m, 1479m, 1385s, 1331s, 1057m, 949w, 706m cm^{-1}.

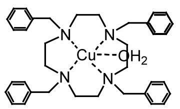
3. Crystallography

Red (cobalt) and blue (copper) crystals were obtained from slow diffusion of ether into complex DMF solution. Crystals have approximate dimensions of $0.20 \times 0.20 \times 0.30$ mm^3 were mounted on a glass fiber. Data were collected on a Rigaku AFC 7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.071069$ Å) using the technique $\omega - 2\theta$ at 20 °C to a maximum 2θ value of 50.0 °C. An empirical correction, applied using the program DIFABS [15], resulted in correction factors ranging from 0.89 to 1.00. The structure was solved by direct methods and expanded using Fourier techniques [16,17]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. All hydrogen atoms were introduced in calculated positions. Scattering factors were taken from the literature [18]. All calculations were performed using the TEXSAN crystallographic software package. Details of data collection and structure refinement are listed in Table 1 [19]. Selected bond lengths and bond distances, angles are listed in Tables 2 and 3, respectively.

4. Results and discussion

The reaction of the tetradentate ligand L with Co(II) and Cu(II) salt in equimolar ratios gave crystalline compounds having the general formula $[ML](NO_3)_2 \cdot nH_2O$ ($n = 0$, $M = Co$; $n = 1.5$, $M = Cu$, see below for suggested structures of these two metal complexes).





The electronic spectra of the complexes were recorded in methanol solution. Absorption maxima in the 200–800 nm region are shown that the copper complex exhibited two strong absorption bands at 208, 262 nm which can be assigned to π–π^* intraligand transitions, and one absorption at 360 ($\varepsilon = 664.5$ M^{-1} cm^{-1}) which correspond to the charge transitions between ligand and metal ion. The spectrum of the Cobalt complex is indicative of a six coordination sphere, giving two bands at 480 ($\varepsilon = 16.5$ M^{-1} cm^{-1}) and 560 ($\varepsilon = 40.2$ M^{-1} cm^{-1}) nm which correspond to the transitions $^4T_{1g(F)} - ^4T_{1g(P)}$ and $^4T_{1g(F)} - A_{2g(F)}$ [20].

Table 3
Bond lengths (Å) and bond angles (°) of $[(C_{36}H_{44}N_4)Cu(OH_2)](NO_3)_2\cdot(H_2O)$

Bond lengths			
Cu–O(1)	2.126(6)	C(9)–C(10)	1.366(12)
Cu–N(1)	2.020(7)	C(10)–C(12)	1.354(12)
Cu–N(2)	2.030(6)	N(2)–C(6)	1.500(10)
O(3)–N(3)	1.217(12)	N(2)–C(4)	1.510(14)
O(4)–N(3)	1.238(12)	C(1)–C(7)	1.534(10)
O(5)–N(3)	1.268(12)	C(14)–C(15)	1.387(11)
O(6)–N(4)	1.258(12)	C(15)–C(16)	1.364(12)
O(7)–N(4)	1.251(13)	C(16)–C(17)	1.376(11)
O(8)–N(4)	1.180(12)	C(17)–C(18)	1.399(11)
N(1)–C(3)	1.440(12)	C(13)–C(18)	1.391(10)
C(3)–C(4)	1.294(13)	C(13)–C(14)	1.398(10)
C(5)–C(13)	1.517(10)	C(11)–C(12)	1.371(11)
C(7)–C(11)	1.354(10)	N(1)–C(2)	1.494(11)
C(7)–C(8)	1.377(11)	N(2)–C(1)	1.516(9)
C(8)–C(9)	1.389(12)	N(2)–C(5)	1.478(9)
Bond angles			
N(2)–Cu–O(1)	101.6(2)	C(8)–C(7)–C(1)	119.1(8)
N(1)–Cu–O(1)	106.7(2)	C(7)–C(8)–C(9)	121.1(8)
N(1)–Cu–N(1)	86.6(4)	C(10)–C(9)–C(8)	119.6(10)
N(1)–Cu–N(2)	151.6(3)	C(12)–C(10)–C(9)	119.4(10)
C(3)–N(1)–C(2)	111.3(9)	C(7)–C(11)–C(12)	121.9(9)
C(3)–N(1)–C(1)	111.5(7)	C(10)–C(12)–C(11)	120.5(9)
C(2)–N(1)–C(1)	111.5(7)	C(18)–C(13)–C(14)	118.8(8)
C(3)–N(1)–Cu	104.0(6)	C(18)–C(13)–C(5)	121.6(8)
C(2)–N(1)–Cu	104.3(5)	C(14)–C(13)–C(5)	119.6(8)
C(1)–N(1)–Cu	113.8(5)	C(15)–C(14)–C(13)	121.0(9)
C(5)–N(2)–C(6)	110.1(7)	C(16)–C(15)–C(14)	119.5(9)
C(5)–N(2)–C(4)	107.5(8)	C(15)–C(16)–C(17)	120.9(9)
C(6)–N(2)–C(4)	117.7(10)	C(16)–C(17)–C(18)	120.3(8)
C(5)–N(2)–Cu	115.2(5)	C(13)–C(18)–C(17)	119.5(8)
C(6)–N(2)–Cu	102.8(5)	N(2)–C(5)–C(13)	116.3(6)
C(4)–N(2)–Cu	103.9(6)	C(11)–C(7)–C(8)	117.5(8)
N(1)–C(1)–C(7)	115.5(7)	C(11)–C(7)–C(1)	123.2(8)
C(4)–C(3)–N(1)	119.9(11)	C(3)–C(4)–N(2)	118.6(10)

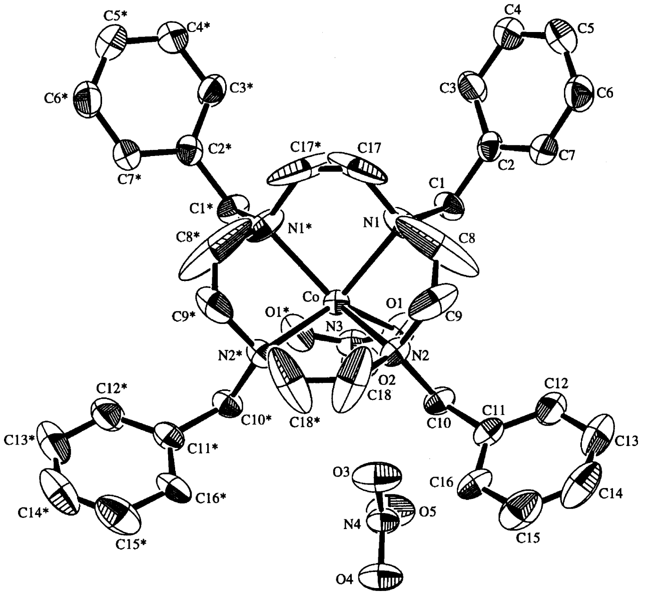


Fig. 1. ORTEP drawing of $[Co(L)(NO_3)](NO_3)$ complex. Ellipsoids are drawn at the 30% probability level, and the hydrogen atoms are omitted for clarity.

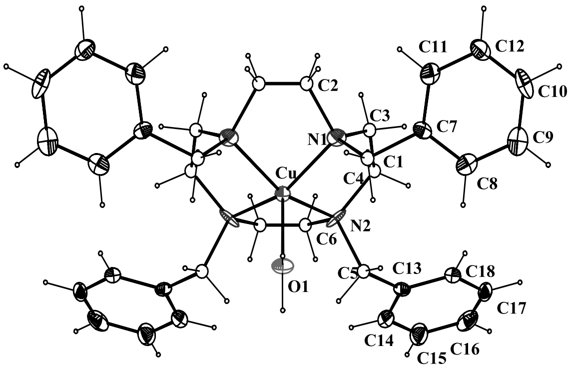


Fig. 2. ORTEP drawing of $[Cu(L)(H_2O)](NO_3)_2H_2O$. Ellipsoids are drawn at the 20% probability level, and the hydrogen atoms and lattice water molecule are omitted for clarity.

4.1. Structure of $[CoL(NO_3)](NO_3)$

X-ray quality crystals of the Co complex were grown from DMF by slow diffusion of Et_2O at room temperature for several days. The solid structure of a packing of discrete $[CoL(NO_3)]^+$ cations, and the other nitrate ion as counter ion, as illustrated in Figs. 1 and 2. The X-ray crystal data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. The central Co atom in the cation is in as six-coordinate environment (N_4O_2), being coordinated by all four nitrogen atoms of the macrocyclic ring and the two oxygen atoms from nitrate which serves as a bidentate ligand. The coordination geometry can be described as a distorted octahedron. Bond lengths of Co–N are almost equal in the 2.212(7)–2.230(7) Å range. Bond lengths for Co–O(1) are 2.142(7) Å. Bond angles between O, Co, N are: O(1)–Co–N(1) 132.6(3)° O(1)–Co–N(2) 92.7(2)° O(1)–Co–N(1) 91.2(3)° O(1)–Co–N(2) 133.0(3)°. The other bond angles around Co atom are slightly larger or smaller than 90°, which indicates that these atoms were nearly perpendicular to each other. O(1) O(1)*, O(2) and N(3) atoms, Co, N(1), N(2), C(8) and C(9) atoms are coplanar. All carbon atoms of phenyl ring are in one plane with the mean deviation 0.0114 and 0.0295 Å. Dihedral angle between these two planes is 32.19°. Four phenyl rings adopt an counterclockwise geometry.

4.2. Structure of $[CuL(H_2O)](NO_3)_2$

The structure of the copper complex consists of $[CuL]^{2+}$, NO_3^- anions and H_2O molecules. The copper atom is five-coordinated, with approximate square pyramidal geometry, by the four nitrogen atoms of the macrocyclic ring and one oxygen atom of water. One water molecule crystallizes in lattice. In the cation, Cu and O(1) reside on a crystallographic imposed mirror plane. Both Cu–N and Cu–O distances are shorter than those of Co–N and Co–O. The unit cell contains two molecule units, and two hydrogen bonds are formed between the coordinated/uncoordinated water molecules and two nitrate counter ions: O(1)–H(1)···O(6) 2.737 Å and O(2)–H(3)···O(7) 2.952 Å.

In these complexes the macrocycle ligand takes a *trans*-I configuration in which all the lone pairs in the four basal nitrogens are oriented on the same side of the macrocyclic ligand plane[12] and the 12-membered ring is folded by the coordination of the metal atoms. The degrees of folding from the Co complex to the Cu complex are presented by both increase in the N(1)–M–N(1) angles and N(1)–M–N(2) angles. All metal ions are high above the mean plane formed by the four basal macrocyclic nitrogens. Four phenyl rings attached with nitrogen atoms are situated on one side of the macrocyclic ligand and imposed the coordinated water or nitrate ion coordinated tightly with the central metal ions.

4.3. Potentiometric titrations

The protonation constants of ligand and stabiltiy constants of Co–L, Cu–L were determined by direct titration of the corresponding mixed solutions (1,4-dioxane-H_2O 70:30 v/v for L and metal complexes with 0.1 M KCl as the supporting material). The results are shown in Table 4. Compared with the known parent ligand Cyclen, the first protonation constants is 1.23 log unit lower. This is ascribed to four benzyl pendent groups, which form superconjugating system with amine atoms and reduce the basicity of them. Marcos et al. reported the existence of four naphthylmethyl pendent groups also low its first protonation constant to 8.64 in parent ligand Cyclam (1,4,8,11-tetraazacyclotetradecane) [21]. Recently, we have reported the first protonation constants of ligand (L′): 1,4,7,10-tetrakis(2-carbamoylethyl)-1,4,7,10-tetraazacyclododecane, is 10.31, also lower than that of Cyclen, because of four carbamoylethyl pendent groups [22]. The overall protonation constants $\log \beta = 16.02$ which is lower than Cyclen ($\log \beta = 21.70$) [23] and L′ ($\log \beta = 18.48$) about 5 or 2 log units, respectively. This indicates that the basicity of this ligand is lower than the other two ligands for lone pairs electron density of nitrogen atom well delocalized in phenyl group via p–π conjugation effect. Fig. 3 showed that three components are formed in the protonation reaction of the ligand.

The stability constants of Co and Cu complexes with this ligand are listed and compared with L′ and L″. The species distribution diagram of Cobalt complexes is shown in Fig. 4. The four coordinated $[CoL]^{2+}$ specie is the most prominent component in the pH range of 2–8. Then the first water molecule attacked the Co–L complex at pH 9.0 and another hydroxide species formed at pH 10.52, which completed the six-coordinated sphere around Co ion. Whereas, the Cu(OH)L species exist in major component of this binary system, which formed started from acidic area (pH < 5). The potentiometric studies showed that these two metal complexes have different bind ability with the ligand and form different type of coordination sphere toward coordination saturation. This ligand shows higher binding ability toward copper(II) than cobalt(II) ions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 153829 and 153830. 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; e-mail: depos-

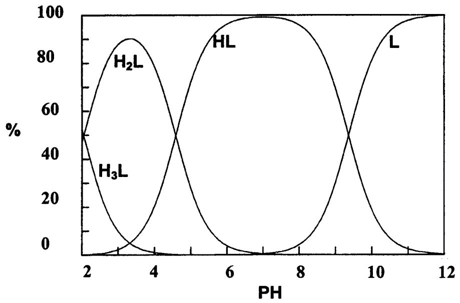


Fig. 3. Species distribution diagram for the ligand.

Table 4
Logarithms of deprotonation constants of ligand and stability constants of complexes ($\mu = 0.100$ M KCl, $t = 25$ °C, under argon)

Equilibrium quotient, K	log K								
	L	L′	Cyclen (L″)	Co–L	Cu–L	Co–L′	Cu–L′	Co–L″	Cu–L″
[HL]/[L][H]	9.37	10.31	10.65						
$[H_2L]/[HL][H]$	4.59	6.83	9.64						
$[H_3L]/[H_2L][H]$	2.06	1.34	1.4						
[ML]/[M][L]				19.79	15.61	17.11	15.00	14.1	24.6
[ML(OH)][H]/[ML]				−9.04		−7.67	−12.3		
$[ML(OH)_2][H]/[ML(OH)]$				−10.52		−6.59			

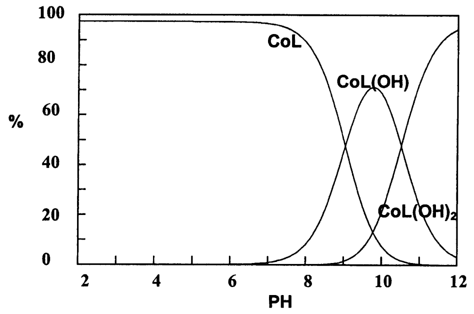


Fig. 4. Species distribution diagrams indicating the species present as function of pH in the system containing 1:1 molar ratio of H_3L^{3+}–Co(II) at 25 °C, $\mu = 0.100$ M (KCl). % = percent of total concentration of the ligand (1×10^{-3} M) set at 100%.

it@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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