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Synthesis and characterization of cobalt(III) tetraaza macrocyclic complexes containing chloro and azido ligands

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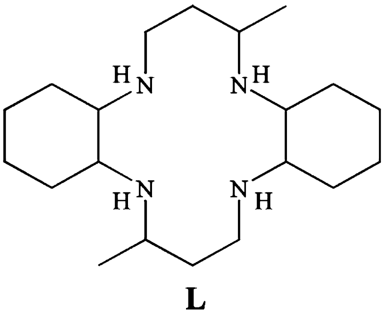
Abstract

The complexes $[Co(L)Cl_2]Cl \cdot 4H_2O$ *(1)* and $[Co(L)(N_3)_2]N_3 \cdot 2H_2O$ *(2)* (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo $[14,4,0^{1.18},0^{7.12}]$docosane) have been synthesized, and structurally characterized by X-ray crystallography, spectroscopy and cyclic voltammetry. The crystal structure of *(1)* is centrosymmetric and the cobalt(III) atom has an axially elongated octahedral geometry with four nitrogen atoms of the macrocycle and two chloride ligands. The cobalt(III) ion in *(2)* is coordinated to four nitrogen atoms from the macrocycle, and two azide ligands in an octahedral environment, which forms the 1D polymer through hydrogen bonding contacts involving the cation, azide anion and solvent water molecules. Electronic spectra of the complexes also exhibit a low-spin octahedral environment. Cyclic voltammetry of the complexes undergoes a one-electron wave corresponding to Co(III)/Co(II) processes. The electronic spectra and electrochemical behaviors of the complexes are significantly affected by the nature of the axial ligands.

Introduction

The application of polyaza macrocycle precursors in the synthesis of transition metal(II) macrocyclic complexes stems mainly from their use as models for protein-metal binding sites in biological systems [1–4], and as selective complexing agents for metal ions [5–8]. Recently, the cyclam and modified cyclam cobalt(III) complexes have been synthesized and structurally characterized by spectroscopy and X-ray crystallography [9–15]. For example, *trans*-$[Co(cyclam)Cl_2]Cl \cdot 4H_2O \cdot 0.47HCl$ [13] and $[Co(H_2ddta)Cl_2](ClO_4)_3 \cdot 2H_2O$ (ddta = 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane) [14] exhibit a low-spin octahedral geometry with four secondary amine nitrogen atoms of the macrocycle and two chloride ligands. However, in a hexaazamacrocyclic cobalt(III) complex $[Co(ddta)](ClO_4)_3$ [14] the cobalt(III) ion has a distorted octahedral geometry with four secondary amines of the macrocycle, and two pendant amines at the axial positions, in which maxima in the electronic spectra are shifted toward higher energy and redox couple shifted to a more negative potential compared with $[Co(H_2ddta)Cl_2](ClO_4)_3 \cdot 2H_2O$. Furthermore, the complex $[Co(dtbh)]PF_6$ (dtbh = 4, 11-diacetamido-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane) [15] reveals a distorted octahedron with four nitrogen atoms of the macrobicycle and two deprotonated carboxylate oxygen atoms of pendant arms.

In the present study, we report the synthesis, properties and crystal structures of cobalt(II) complexes, $[Co(L)Cl_2]Cl \cdot 4H_2O$ *(1)* and $[Co(L)(N_3)_2]N_3 \cdot 2H_2O$ (*2*) (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo$[14,4,0^{1.18},0^{7.12}]$docosane). To understand the nature of the axial ligands, the solid state X-ray crystal structures of the complexes are determined and compared to their solution structures by the electronic absorption spectroscopy and cyclic voltammetry.



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Experimental

Materials and physical measurements

All reagents and solvents for syntheses and analyses were of analytical grade and were used as received.

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The macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane (L) was prepared according to the literature method [16]. I.r. spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. The solution electronic and diffuse reflectance spectra were obtained on a Jasco V-550 spectrophotometer. Elemental analyses of C, H and N were carried out on a Perkin-Elmer CHN-2400 analyzer. Electrochemical measurements were accomplished with a three electrode potentiostat BAS-100 BW system. A 3-mm Pt disk was used as the working electrode. The counter electrode was a coiled Pt wire and a Ag/AgCl electrode was used as a reference electrode. Cyclic voltammetric data were obtained in DMSO solution with 0.10 M Et_4NClO_4 (TEAP) as supporting electrolyte at 20.0 ± 0.1 °C.

Synthesis of [Co(L)Cl_2]Cl · $4H_2O$ (1)

To a MeOH solution (20 cm^3) of $CoCl_2 \cdot 6H_2O$ (476 mg, 2.0 mmol) was added a MeOH solution (10 cm^3) of ligand (672 mg, 2.0 mmol). The mixture was heated to reflux for 1 h and then cooled to room temperature. Concentrated HCl was added dropwise until the red-brown solution turned green. Air was then bubbled through the solution for 2 h. The solution was filtered and allowed to stand for a few days, a quantity of green crystals precipitates, which were filtered, and recrystallized from a hot H_2O/MeOH (1:1 v/v, 10 cm^3) mixture. Yield: 73%. (Found: C, 41.9; H, 8.5; N, 9.7. $C_{20}H_{48}Cl_3CoN_4O_4$; calcd.: C, 41.9; H, 8.4; N, 9.8%). I.r. (KBr, cm^{-1}): 3424(s), 3184(s), 2943(s), 1654(w), 1625(w), 1454(m), 1427(w), 1388(w), 1370(w), 1357(w), 1305(w), 1270(w), 1155(w), 1094(s), 1071(s), 1009(m), 971(m), 901(m), 840(w), 650(w), 555(w), 451(w).

Synthesis of [Co(L)$(N_3)_2$]N_3 · $2H_2O$ (2)

To a H_2O solution (20 cm^3) of [Co(L)Cl_2]Cl · $4H_2O$ (287 mg, 0.5 mmol) was added NaN_3 (33 mg, 0.5 mmol), then the mixture was heated to the reflux temperature, during which time for 1 h, the solution changed from green to red. After the solution was allowed to stand at room temperature over a period of several days, the red crystals formed. The product was filtered and recrystallized from a hot H_2O/CH_3CN (1:1 v/v, 10 cm^3) mixture. Yield: 65%. (Found: C, 43.2; H, 7.9; N, 32.6. $C_{20}H_{44}CoN_{13}O_2$; calcd.: C, 43.1; H, 8.0; N, 32.7%). I.r. (KBr, cm^{-1}): 3422(m), 3174(m), 2940(m), 2064(s), 2022(s), 1646(w), 1498(m), 1458(m), 1389(w), 1351(m), 1311(w), 1223(w), 1186(w), 1096(m), 1009(m), 976(m), 911(w), 850(w), 659(w), 553(w), 457(w).

X-ray crystallography

Intensity data for compounds *(1)* and *(2)* were measured on a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Accurate cell parameters and an orientation matrix were determined by the least-squares fit of 25 reflections. The intensity data were collected by the $\omega - 2\theta$ technique and corrected for Lorentz and polarization effects. An empirical absorption correction was applied with the SADABS program [17]. The structures were solved by direct methods [18], and the least-squares refinements of the structures were performed by the SHELXL-97 program [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C atoms with $U_{iso}(H) = 1.2U_{eq}$(C or N). Hydrogen atoms Ow(2) and Ow(4) for *(1)* were not found. Crystallographic and experimental details of structural analyses for complexes *(1)* and *(2)* are summarized in Table 1.

Results and discussion

Description of the structures

An ORTEP drawing of *trans*-[Co(L)Cl_2]Cl · $4H_2O$ *(1)* with the atomic numbering scheme is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The unit cell contains cation $[Co(L)Cl_2]^+$, one Cl^- anion, and four H_2O molecules. The macrocyclic ligand skeleton of the molecular cation contains two cyclohexane rings and two gauche five-membered and two chair six-membered chelate rings with most stable *trans*-III (*R,R,S,S*) conformation in the solid state. There are two half molecules and each of the complete molecules is composed by the inversion center of symmetry. The crystal structure of *(1)* reveals a six-coordinated octahedral geometry with bonds from the cobalt(III) ion to the four secondary amine nitrogen atoms of the macrocycle and to the two axial chloride ligands. The two axial Co–Cl distances are similar [2.264(2) and 2.267(2) Å], and longer than the average distance of Co(1)–N_4 and Co(2)-N_4 plane [2.002 and 1.997 Å], giving an axially elongated octahedral geometry. The Co–N bond distance values are comparable with those observed in *trans*-[Co(cyclam)Cl_2]Cl · $4H_2O$ · 0.47HCl [1.974(2) and 1.981(2) Å] [13] and *cis*-[Co(cyclam)(en)]Cl_3 · $3H_2O$ [1.996(2) Å] [9]. The N–Co–N angles of the six-membered chelate ring are much larger than those of the five-membered chelate ring. The axial Co–Cl bond is not perfectly perpendicular to the CoN_4 plane with the Cl–Co–N angles from 86.9(1)° to 93.1(1)°.

An ORTEP drawing of [Co(L)$(N_3)_2$]N_3 · $2H_2O$ *(2)* with the atomic numbering scheme is shown in Figure 2 and the selected bond lengths and angles are listed in Table 3. The structure consists of $[Co(L)(N_3)_2]^+$ cation, one N_3^- anion, and two H_2O molecules. The macrocyclic ligand skeleton in *(2)* adopts the most stable *trans*-III (*R,R,S,S*) conformation. The crystal structure of (2) shows that the cobalt(III) ion is coordinated by four nitrogen atoms of the macrocycle and two nitrogen atoms of the azide ligand in a distorted octahedral geometry. The average Co–N (macrocycle) dis-

Table 1. Crystallographic data

	(1)	*(2)*
Empirical formula	$C_{20}H_{48}Cl_3CoN_4O_4$	$C_{20}H_{44}CoN_{13}O_2$
Formula weight	573.90	557.61
Temperature (K)	293(2)	293(2)
Crystal color/habit	Block/green	Rod/red
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/c$
Unit cell dimensions		
a (Å)	11.369(6)	9.5904(5)
b (Å)	11.556(6)	19.5673(9)
c (Å)	11.792(7)	13.8914(7)
α (°)	115.58(1)	
β (°)	102.67(1)	99.241(1)
γ (°)	99.54(1)	
V (Å^3)	1302.2(12)	2573.0(2)
Z	2	4
D_{calc}(Mg m^{-3})	1.464	1.439
Absorption coefficient (mm^{-1})	1.000	0.713
F(000)	612	1192
Crystal size (mm)	$0.32 \times 0.19 \times 0.11$	$0.25 \times 0.14 \times 0.07$
θ range (°)	1.92–28.34	1.81–28.34
Limiting indices	$-15 \le h \le 15$, $-15 \le k \le 15$, $-15 \le l \le 15$	$-12 \le h \le 12$, $-25 \le k \le 26$, $-18 \le l \le 18$
Reflection collected/unique	16917/6415 ($R_{int} = 0.0971$)	26370/6406 ($R_{int} = 0.0484$)
Absorption correction	SADABS	SADABS
Max./min. transmission	0.8923 and 0.3535	0.9500 and 0.7699
Data/restraints/parameters	6415/0/304	6406/0/349
Goodness of fit on F^2	1.009	1.038
Final R indices ($I > 2\sigma(I)$)	$R_1^a = 0.0824$, $wR_2^b = 0.2012$	$R_1^a = 0.0396$, $wR_2^b = 0.0895$
R indices (all data)	$R_1 = 0.1415$, $wR_2 = 0.2515$	$R_1 = 0.0790$, $wR_2 = 0.1103$
Largest difference peak and hole (eÅ^{-3})	2.494 and −1.047	0.723 and −0.338

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

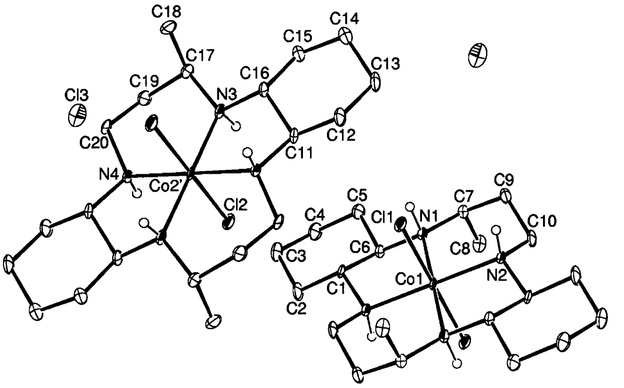

Fig. 1. An ORTEP diagram of $[Co(L)Cl_2]Cl \cdot 4H_2O$ *(1)* with the atom-numbering scheme (30% probability ellipsoids shown). The H_2O molecules and hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for $[Co(L)Cl_2]Cl \cdot 4H_2O$ *(1)*^{a}

Bond lengths			
Co(1)–N(1)	2.022(4)	Co(1)–N(2)	1.982(4)
Co(1)–Cl(1)	2.264(2)	Co(2)–N(3)	2.018(4)
Co(2)–N(4)	1.975(4)	Co(2)–Cl(2)	2.267(2)
Bond angles			
N(1)–Co(1)–N(2)	94.5(2)	N(1)–Co(1)–N(2)^i	85.5(2)
N(1)–Co(1)–Cl(1)	87.0(1)	N(2)–Co(1)–Cl(1)	87.5(1)
N(1)^i–Co(1)–Cl(1)	93.0(1)	N(2)^i–Co(1)–Cl(1)	92.5(1)
N(3)–Co(2)–N(4)	94.6(2)	N(3)–Co(2)–N(4)^{ii}	85.4(2)
N(3)–Co(2)–Cl(2)	86.9(1)	N(4)–Co(2)–Cl(2)	87.4(1)
N(3)^{ii}–Co(2)–Cl(2)	93.1(1)	N(4)^{ii}–Co(2)–Cl(2)	92.6(1)

^{a}Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$.

tance of 1.996(2) Å is very closed to that found in *(1)*. The average Co–N (azido) distance of 1.947(2) Å is similar to those found in azido cobalt(III) complexes *mer*-$[Co(dmp)_3(N_3)_3]$ [dmp = 3,4-dimethylpyridine; 1.931(4) to 1.959(4) Å] [20] and *trans*-$[Co(tet)_3(N_3)_2]ClO_4$ [tet = 1,10-diamino-4,7-diazadecane; 1.949(3) and 1.959(3) Å] [21] in which the cobalt(III) ion adopts a distorted octahedral geometry. Also, the axial Co–N (azido) linkage is bent slightly off the perpendicular to the CoN_4 plane by 0.1–5.7°. The coordinated azido groups which act as a monodentate ligand are slightly asymmetric [N(5)–N(6) = 1.193(3) Å and N(6)–N(7) = 1.162(3) Å; N(8)–N(9) = 1.185(3) Å and N(9)–N(10) = 1.159(3) Å] and linear within the experimental error [N(5)–N(6)–N(7) = 175.9(2)° and N(8)–N(9)–N(10) = 176.3(3) °]. The Co–N(5)–N(6) and Co–N(8)–N(9) angles related to the azide ligand are 132.8(2)° and 131.2(2)°, respectively. Interestingly, the secondary amines of the macrocycle are hydrogen bonded to nitrogen atoms of the azide ligand [N(1)···N(7)^{ii} 3.217(3) Å, 161(2)°; N(2)···N(6)^{iii} 3.362(3) Å, 121(2)°; N(3)···N(10)^{iii} 3.341(3) Å, 155(2)°; N(4)···N(9)^i 3.339(3) Å, 119(2)°; symmetry codes: (i) x, y, z; (ii) $x, -y+3/2, z+1/2$; (iii) $x, -y+3/2, z-1/2$]. Further-

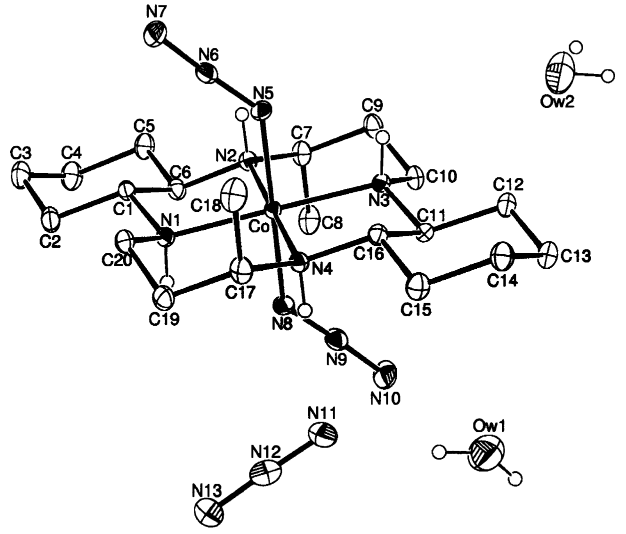

Fig. 2. An ORTEP diagram of $[Co(L)(N_3)_2]N_3 \cdot 2H_2O$ *(2)* with the atom-numbering scheme (30% probability ellipsoids shown). The hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for $[Co(L)(N_3)_2]$-$N_3 \cdot 2H_2O$ (*2*)

Bond lengths			
Co–N(1)	1.980(2)	Co–N(2)	2.002(2)
Co–N(3)	1.991(2)	Co–N(4)	2.012(2)
Co–N(5)	1.945(2)	Co–N(8)	1.949(2)
N(5)–N(6)	1.193(3)	N(6)–N(7)	1.162(3)
N(8)–N(9)	1.185(3)	N(9)–N(10)	1.159(3)
N(11)–N(12)	1.183(3)	N(12)–N(13)	1.186(3)
Bond angles			
N(1)–Co–N(2)	85.1(1)	N(1)–Co–N(3)	179.5(1)
N(1)–Co–N(4)	94.9(1)	N(2)–Co–N(3)	95.4(1)
N(2)–Co–N(4)	179.8(1)	N(3)–Co–N(4)	84.6(1)
N(5)–Co–N(1)	95.6(1)	N(5)–Co–N(2)	88.9(1)
N(5)–Co–N(3)	84.7(1)	N(5)–Co–N(4)	91.4(1)
N(5)–Co–N(8)	179.4(1)	N(8)–Co–N(1)	84.3(1)
N(8)–Co–N(2)	90.6(1)	N(8)–Co–N(3)	95.4(1)
N(8)–Co–N(4)	89.2(1)	Co–N(5)–N(6)	132.8(2)
Co–N(8)–N(9)	131.2(2)	N(5)–N(6)–N(7)	175.9(2)
N(8)–N(9)–N(10)	176.3(3)	N(11)–N(12)–N(13)	179.2(3)

more, the H_2O molecules found in the lattice also form hydrogen bonds with nitrogen atoms of the azide ligand, and with the other H_2O inclusion [Ow(1)···N(10)^{i} 3.076(4) Å, 89(3)°; Ow(1)···N(11)^{i} 3.081(4) Å, 172(4)°; Ow(2)···N(13)^{iv} 2.991(4) Å, 169(4)°; Ow(1)···Ow(2)^{ii} 2.939(5) Å, 133(4)°; symmetry codes: (i) x, y, z; (ii) x, $-y + 3/2$, $z + 1/2$; (iv) $x - 1$, $-y + 3/2$, $z - 1/2$]. This interaction, as shown in Figure 3 and Table 4, gives rise to the one-dimensional hydrogen-bonded polymer.

Spectral and electrochemical properties

The i.r. spectra of complexes show bands at 3174 and 3184 cm^{-1}, which are assigned to the ν(N–H) of the coordinated secondary amines of the macrocycle. Two strong bands at 2022 and 2064 cm^{-1} in *(2)* were assigned to $\nu_{as}(N_3)$ stretching of the coordinated and uncoordinated azide ligands [22], which are in agreement with the crystal structure of *(2)*. The spectroscopic data of the complexes are listed in Table 5. The electronic spectra of *(2)* in the solid and DMSO solution exhibit two bands in the range 362–370 and

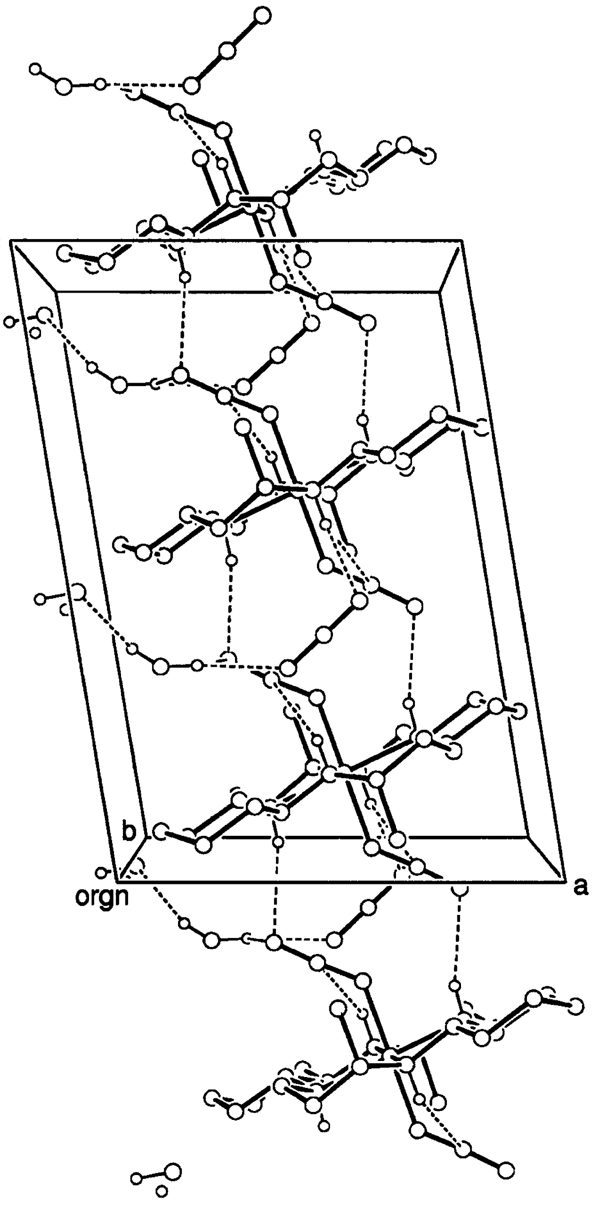

Fig. 3. View of 1D hydrogen-bonded polymeric chain structure of $[Co(L)(N_3)_2]N_3 \cdot 2H_2O$ *(2)*.

Table 4. Hydrogen-bond parameters (Å, °) for $[Co(L)(N_3)_2]N_3 \cdot 2H_2O$ $(2)^{a}$

D-H···A	D-H (Å)	H···A (Å)	D-A (Å)	D-H···A (°)
N(1)–H(21)···N(7)^{ii}	0.86(3)	2.39(3)	3.217(3)	161(2)
N(2)–H(22)···N(6)^{iii}	0.88(3)	2.82(2)	3.362(3)	121(2)
N(2)–H(22)···N(13)^{i}	0.88(3)	2.18(3)	3.030(3)	162(2)
N(3)–H(23)···N(10)^{iii}	0.86(2)	2.54(3)	3.341(3)	155(2)
N(4)–H(24)···N(9)^{i}	0.88(2)	2.82(3)	3.339(3)	119(2)
Ow(1)–H(25A)···N(11)^{i}	0.91(4)	2.18(4)	3.081(4)	172(4)
Ow(1)–H(25A)···N(10)^{i}	0.91(4)	2.96(4)	3.076(4)	89(3)
Ow(2)–H(26A)···N(13)^{iv}	0.90(4)	2.10(5)	2.991(4)	169(4)
Ow(1)–H(25B)···Ow(2)^{ii}	0.80(4)	2.33(5)	2.939(5)	133(4)

[a] Symmetry codes: (i) x, y, z; (ii) x, $-y + 3/2$, $z + 1/2$; (iii) x, $-y + 3/2$, $z - 1/2$; (iv) $x - 1$, $-y + 3/2$, $z - 1/2$.

Table 5. Electronic spectral and cyclic voltammetric data of macrocyclic cobalt(III) complexes

Complex	Electronic spectrum λ_{max}, nm (ε = M^{-1} cm^{-1})	Potentials (V) *Vs.* Ag/AgCl Co(III)/Co(II)
[Co(cyclam)Cl$_2$]Cl· H$_2$O[a]	386(56)[c], 458(24)[c], 617(35)[c]	
[Co(cyclam)(N$_3$)$_2$]ClO$_4$[a]	575(430)[c]	
[Co(L)Cl$_2$]Cl· 4H$_2$O (1)	366(2.45 × 10^3)[d], 646(295)[d], 363[e], 638[e]	− 0.16
[Co(L)(N$_3$)$_2$]N$_3$· 2H$_2$O (2)	370(9.72 × 10^3)[d], 575(336)[d], 362[e], 568[e]	− 0.54(i)[f]
[Co(H$_2$ddta)Cl$_2$](ClO$_4$)$_3$· 2H$_2$O[b]		− 0.03(i)[f]
[Co(ddta)](ClO$_4$)$_3$[b]		− 0.79

L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,0$^{1.18}$,0$^{7.12}$]docosane; ddta = 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane.

[a] Ref. [10].

[b] Ref. [14].

[c] MeOH.

[d] DMSO.

[e] diffuse reflectance.

[f] i = irreversible.

568–575 nm, which are very close to those found for [Co(cyclam)(N$_3$)$_2$]ClO$_4$ [10]. The first band is due to $^1A_{1g} \rightarrow {}^1T_{2g}$ in a low-spin octahedral cobalt(III) complex which is not affected by lowering of the symmetry. Owing to the high intensity of this band it may be mixed with the ligand-to-metal charge transfer transition. The lower energy absorption band is believed to be $^1A_{1g} \rightarrow {}^1T_{1g}$ transition for low-spin d^6 ion under O$_h$ symmetry. However, the visible spectra of the green complex *(1)* display the characteristic splitting of the $^1T_{1g}$ excited state to a $^1A_{2g}$ and ^1E_g state under the influence of the tetragonally distorted ligand field, which is consistent with the crystal structure of *(1)*. Thus, the visible absorption bands at 638 (solid) and 646 nm (DMSO) in (1) are assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition. Similar result was observed for related cyclam complex [Co(cyclam)Cl$_2$]Cl · H$_2$O [10].

Cyclic voltammetric data for the cobalt(III) complexes in 0.10 M TEAP-DMSO solution are listed in Table 5. Cyclic voltammetry of the complexes undergoes a reversible or irreversible one-electron wave corresponding to Co(III)/Co(II) processes. Although complexes *(1)* and *(2)* have a similar average Co–N (macrocycle) bond distance, the reduction potential for *(1)* is considerably more positive than that of *(2)* indicating that complex *(1)* makes reduction easier. This result may be reflected by the field strength of the axial ligands as observed in the hexaazamacrocyclic cobalt(III) complexes [Co(H$_2$ddta)Cl$_2$](ClO$_4$)$_3$ · 2H$_2$O and [Co(ddta)](ClO$_4$)$_3$ [14].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 612126 for *(1)* and 612127 for *(2)*. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2,1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.uk or http://www.ccdc.cam.ac.uk).

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