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Synthesis and stability of new hexaazamacrocyclic dinuclear cobalt complexes and its oxidation reactions

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Abstract

Homodinuclear cobalt complexes with a new 26-membered unsymmetric macrocyclic ligand: 3,6,10,18,22,25,-hexaaza-31,32-dihydroxy-14,29-dimethyl-tricyclo[25,3,1,1^{11,17}] dotriaconta-l(30),12,14,16(32),27,28-hexaene (L or BTBP), have been synthesized and characterized with elemental analysis, FAB-MS and X-ray. The ligand maintains preorganized dinuclear integrity for cobalt(II) complexes, while facilitating the formation of non-bridged dicobalt centers. Potentiometric equilibrium studies indicate that a variety of protonated, mononuclear and dinuclear complexes are formed with Co(II) from pH 2 through 12 in aq. solution. The stability constants and species distribution as a function of pH of the 1:1 and 1:2 [ligand: Co(II)] complexes were determined in KCl supporting electrolyte ($\mu = 0.100$ M) at 25 °C. Dinuclear cobalt(II) complex could form a μ-peroxo adduct at 1 atm oxygen atmosphere with the oxygenation constant log $K_{O_2} = 3.19$. The neutral homodinuclear complexes: [Co$_2$C$_{28}$H$_{44}$N$_6$O$_2$(NO$_3$)$_2$]·12H$_2$O has been synthesized and its crystal structure has been reported with triclinic system, $a = 8.3376(5)$, $b = 9.4501(6)$, $c = 14.1028(9)$ Å, $\alpha = 73.9100(2)$, $\beta = 73.4940(2)$, $\gamma = 87.7310(2)°$ and $Z = 1$. Each cobalt(II) ion is complexed by half of the coordination sites of the dinucleating macrocycle, and the anionic nitrate enters into the coordination sphere and completes a six-coordinated octahedron.
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Keywords: Hexaazamacrocyclic ligand; Cobalt; Dinuclear complexes; Potentiometry

1. Introduction

In biomimetic and abiotic processes, the binding, transport and activation of molecular oxygen by metal complexes are of great interest.[1–3] Co(II) complexes with polyamine ligands containing binding units suited for the coordination of a single metal ion or for the dinuclear centers have proved very useful. The structure of these synthetic dioxygen carriers, the kinetics and thermodynamics of their formation is affected by the nature of the ligand. The use of polynucleating ligands represents an evolution in synthetic Co(II) dioxygen carriers. These ligands contain sufficient number of oxygen and nitrogen donor atoms to coordinate more than one Co(II) ion and can act as biomimetic models of natural non-heme types carriers, such as hemerythrin and hemocyanin. Martell et al. [4] examined the Co(II) complexes with the dinucleating ligands OBISTREN, BISTREN, BIDIEN and BISBAMP in aqueous solution and obtained several interesting results. The Co$_2$(II)BISTREN complex shows an unexpected low affinity with O$_2$ and a very slow metal-centered degradation to Co$_2$(III)BISTREN complex. As a result, the Co$_2$(II)BISTREN(μ-O$_2$)(μ-OH) complex is a very good oxygen carrier and uptake-release of O$_2$ are run many times by simply heating and cooling its aqueous solutions. More recently, Bosnich pointed out that a suitable oxygenation catalyst has oxygen bound to one metal center via end-on coordination similar to oxyhemerythrin [5].

As a continuing investigation of macrocyclic dinuclear cobalt complex, this report describes the synthesis of a new homodinuclear cobalt complex with a new 26-membered macrocyclic ligand (BTBP) and thermodynamic characterization of its oxygenated adduct. X-ray also has structurally determined this homodinuclear cobalt complex.

2. Results and discussion

2.1. Stability of cobalt(II) mononuclear complexes

The potentiometric data obtained from solutions containing $H_2L\cdot 6HBr$ and cobalt ions are illustrated in Fig. 1. The inflection at $a = 4$ indicates the formation of the mononuclear and dinuclear complexes, respectively. The pH titration curves were employed to calculate 1:1 and 1:2 ligand:metal binding constants. The stability constants involving protonated and deprotonated Co(II) species are shown in Table 1. For mononuclear systems, four protonated major species $[CoH_4L]^{4+}$, $[CoH_3L]^{3+}$, $[CoH_2L]^{2+}$ and $[CoHL]^+$ were identified with fairly high stability constants. [CoL] becomes major component only at more basic region, with high concentrations when the pH of the solution is higher than 11. The other four protonated species: $[CoH_4L]^{4+}$, $[CoH_3L]^{3+}$, $[CoH_2L]^{2+}$ and $[CoHL]^+$ reach their maximum concentration (89.3, 78.0, 70.6 and 69.9%) at pH 4.9, 7.1, 8.8 and 10.3, respectively. In the 1:1 system, no dinuclear species were found. This point is different from Co-BDBPH. In that case, Co(II) forms dinuclear protonated species-$[Co_2HL]^{2+}$ at very low pH. The ring size of BTBP is larger than that of BDBPH though they have same coordination donors. The positive charges existing in protonated species of BTBP (Fig. 2) are distributed along macrocyclic skeleton in six amine nitrogens. So the higher positive protonated species could be stable in solution.

The formation constant of log $K_{[CoL]}$ is 18.02 which is larger than that of BDBPH log $K_{[CoL]} = 13.35$ [6] and that of OBISDIEN(L″), log $K_{[CoL″]} = 9.73$ [7]. As the

total basicity of BTBP is higher than BDBPH, the amine group in the macrocyclic cavity could coordinate to central metal ions more easily. As far as OBISTREN, though it has similar side chains with same six amine nitrogen donors, BTBP has two phenolic heads in the 26-membered macrocyclic skeleton, which largely increases the affinity to metal ions compared with the ether oxygen in OBISDIEN (see Scheme 1 for the structural information of L′ and L″).

2.2. Stabilities of cobalt(II) dinuclear complexes

For the 1:2 system, two strong inflections occur at $a = 4$, 8 indicating that dinuclear ferric complexes formed stepwise. The first inflection appeared at $a = 4$ in titration curve in Fig. 1 indicating that the first formed species is a tetraprotonated mononuclear complex, $[CoH_4L]^{4+}$, as a major component in low pH region. Its maximum concentration appears at pH 4.6 with 96.2%. The data in Table 2 show that the addition of a second metal ion to [CoL] to form $[Co_2L]^{2+}$ is characterized by a much lower stability constant than that of [CoL], because of the destabilization resulting from the coulombic repulsion between the two metal ions in the limited macrocyclic cavity. Martell et al. also reported this trend in similar works on Co(II) toward hexaazamacrocyclic ligands BDBPH and OBISTREN, the stability constants changed from 13.35 (log $K_{[CoL]}$) to 11.12 (log $K_{[Co2L']^{2+}}$) and from 9.73 (log $K_{[CoL″]}$) to 2.7 (log $K_{[Co2L″]^{2+}}$). The formation constant of the dinuclear complex is log $K_{[Co2L]^{2+}} = 9.23$ compared with L′ log $K_{[Co2L']^{2+}} = 11.12$, slightly lower than L′ by 1.89 logrithm units. Combined two more carbon atoms into macrocyclic skeleton of L could reduce the rigidity and make the cavity not symmetric as BDBPH, would lower the stability of dinuclear cobalt complexes. The species distribution diagram of the system H_8L–2Co is shown in Fig. 3. It is seen that the mononuclear $[CoH_4L]^{4+}$ and $[CoH_3L]^{3+}$ complexes predominate from pH 4 to 7. The other mononuclear complexes exit at more basic region with the percentage around 7.5%. Then the second cobalt enters into the macrocyclic cavity to form the protonated dinuclear cobalt complex $[Co_2HL]^{3+}$, it reaches its maximum concentration (29.7%) at pH 6.8. Neutral dinuclear complexes start to form from pH > 7, and reach their highest concentration at pH 9.5 (93.0%). The first water molecule coordinated with cobalt ion forms hydroxo complex $[Co_2(OH)L]^+$ when pH is higher than 10. It overlaps with neutral dinuclear species and reaches a maximum concentration 77.0% at pH 12. The stability constants of 2:1 Co(II) complexes with fully deprotonated BTBP, Co_2L, is 9.23, which is slightly higher than Fe(II)$_2$L (log[Fe$_2$L]/[Fe][FeL] = 9.02), Fe(III)$_2$L (log[Fe$_2$L]/[Fe][FeL] = 7.41) [8] and greatly lower than Cu$_2$L (log[Cu$_2$L]/[Cu][CuL] = = 21.95) [9]. Co(II) ion has
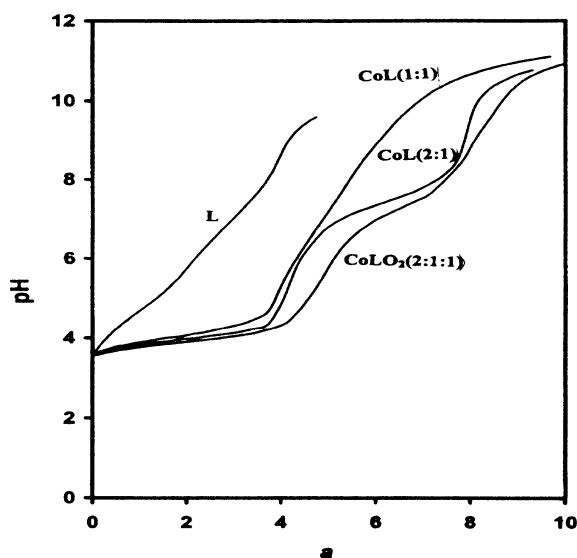

Fig. 1. The titration curve of Co–H_8L^{6+} systems.

Table 1
Stepwise stability constants for the L–Co(II) system [$\mu = 0.10$ M (KCl), 25 °C, under argon]

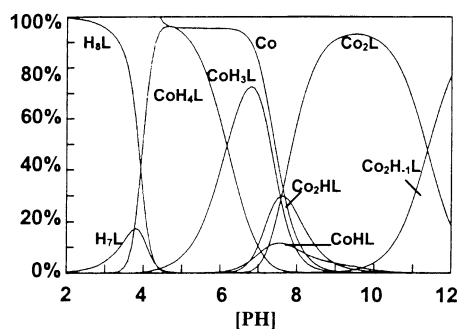| Stepwise quotient, K	BTBP log K [a]	BDBPH log K [a]	OBISDIEN log K [a]	BISBAMP log K [a]
[CoL]/[Co][L]	18.02	13.35	9.73	9.05
[CoHL]/[CoL][H]	10.99	–	7.58	7.12
[CoH$_2$L]/[CoHL][H]	9.54	–	5.97	–
[CoH$_3$L]/[CoH$_2$L][H]	7.99	–	–	–
[CoH$_4$L]/[CoH$_3$L][H]	6.17	–	–	–
[CoL]/[Co(OH)L][H]	–	–	–	9.97
[Co$_2$L]/[CoL][Co]	9.23	11.12	2.7	3.00
[Co$_2$HL]/[Co$_2$L][H]	7.60	10.32	–	–
[Co$_2$H$_2$L]/[Co$_2$HL][H]	–	5.69	–	–
[Co$_2$L]/[Co$_2$(OH)L][H]	−11.38	−6.34	–	−7.90
[Co$_2$(OH)L]/[Co$_2$(OH)$_2$L][H]	–	−10.56	–	–

–, Species not found.
[a] Estimated error = ± 0.02–0.04.

Fig. 2. Species distribution diagrams indicating the species present as a function of p[H] in the system containing a 2:1 molar ratio of Co–H$_8$L^{6+} at 25 °C, $\mu = 0.100$ M (KCl) under argon. % = percent of total concentration of ligand (1×10^{-3} M) set at 100%. The ligand and minor species (maximum content less than 5%) are omitted for clarity.
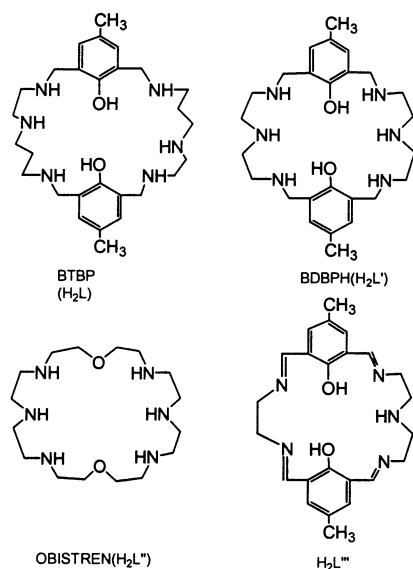
Scheme 1.

high coordination number compared with Cu(II) ion and easily to form an octahedral coordination sphere. The dinuclear-hydroxylated species is very stable, indicating that the complexes present a good tendency to coordinate additional species from the medium. This is a promising starting point for the use of this compound as an oxygen binder.

2.3. Oxygenation and stability of dinuclear complexes

As expected, this dinuclear compound is able to bind molecular oxygen giving rise to the formation of stable oxygenated complexes. When the titration has been done under 1 atm purified oxygen, the curve in Fig. 1 has an inflection when the a value is near 4.5, which indicates the formation of tetraprotonated mononuclear species [CoH$_4$L]$^{4+}$; it overlaps a little with other mononuclear species. [CoH$_3$L]$^{3+}$ is the major constitute in acid area. Two dinuclear protonated species also have been produced, occupying a small percentage of species distribution. The formation of neutral oxygenated dinuclear species: [Co$_2$LO$_2$]$^{2+}$ is slow. It takes 1–2 h to reach each equilibrium point. Oxygen complexes start to appear at pH 6. The first oxygen species-[Co$_2$LO$_2$]$^{2+}$ reach its highest concentration-75.1% when the pH increases to 8.2. Then [Co$_2$L(OH)O$_2$]$^+$ becomes the major species in the pH range from 9 to 12.

Formula (1) and (2) represent the non-hydroxo and mono-hydroxo dioxygen complexes with ligand and the equilibrium constants defined by Eqs. (1) to (3) are reported in Table 2. The oxygen complex formation of this ligand and cobalt ion is log $K_{O_2} = 3.19$ which is slightly smaller than the Co-OBISDIEN. This can be accounted for the existence of two phenolate heads in this ligand, which increased the rigidity of the ligand and makes it somewhat difficult to change to accommodate the molecular oxygen. Meanwhile, in Co-OBISDIEN-Oxygen system, the species [Co$_2$L″O$_2$]$^{4+}$ (L″ = OBISDIEN) is never more than a minor constituent in

Table 2
Stepwise stability constants for the L–Co(II) systems [$\mu = 0.10$ M (KCl), 25 °C, in the presence of O_2]

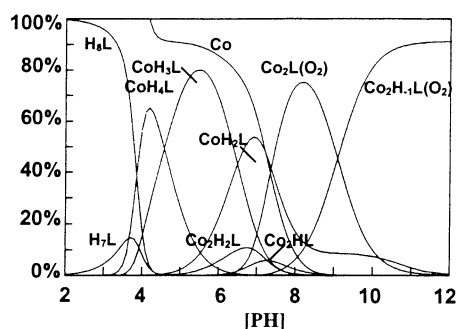| Stepwise quotient, K	BTBP log K [a]	BDBPH log K [a]	OBISDIEN log K [a]	[27]aneN$_9$ log K [b]
$[Co_2L(O_2)]/[Co_2L]PO_2$	3.19	13.29	–	5.8
$[Co_2L(O_2)]/[Co_2L(O_2)(OH)][H]$	−9.09	–	3.29	−5.7
$[Co_2L(O_2)(OH)]/[Co_2L(O_2)(OH)_2][H]$		–	−8.25	
$[Co_2L(O_2)_2(OH)]/[Co_2L(O_2)(OH)_3][H]$			−9.36	
$[Co_2L(O_2)(OH)]/[Co_2L(OH)]PO_2$	0.9			6.8

–, Species not found.
[a] Estimated error = ±0.02–0.04.
[b] In 0.15 M $NaClO_4$.

Fig. 3. Species distribution diagrams indicating the species present as a function of p[H] in the system containing a 2:1 molar ratio of Co–H_8L^{6+} at 25 °C, $\mu = 0.100$ M (KCl) under oxygen. % = percent of total concentration of ligand (1×10^{-3} M) set at 100%. The ligand and minor species (maximum content less than 5%) are omitted for clarity.
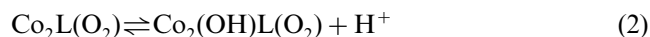
solution. This is ascribed to low stability resulting from steric effects and the strong tendency of the dinuclear Co(II) complex to combine with bridging hydroxide ions, which take up the coordination sites that would otherwise be occupied by the bridging peroxo group of the dioxygen complex. The bridging groups and the basic nitrogen donor groups of the dioxygen complex of Co-OBISDIEN initially formed account for only five of the required six coordination of the metal ion. That sixth position is probably occupied by water molecules, which is indicated by the facile dissociation of two protons, resulting in the formation of a dihydroxo- or trihydroxo- dioxygen complexes at higher pH. But the BTBP can serve as an octadentate (N_6O_2) ligand when the dinuclear complexes are formed. In this dinuclear crystal structure, it clearly can be found that each cobalt ion only occupied half of the coordination sphere of the cavity with two NO_3 ion serving as additional ligand. So when this compound binds with molecular oxygen, the fifth binding site will be served by μ-peroxo oxygen. Then the sixth coordination site will be satisfied with bridged hydroxide ion.

It is quite interesting that O_2 and OH^- did not show a cooperativity in the binding to the dicobalt complexes of the macrocyclic ligands as Bianchi et al. reported [10a,10b]. In their work, [10] the direct interactions via

hydrogen bonding between O_2 and OH^- in the di-Co-[27]aneN$_9$ complexes is assumed. In support of this point, monodentate molecular oxygen coordinated to one cobalt ion via end-on fashion has been suggested. Compared with this system, the oxygenation constant of hydroxide species $[Co_2(OH)L]$ is calculated to 7.94 (log $K = 0.9$). This value is not comparable with oxygenated species-$[Co_2(O_2)L]$, and the logrithm of its hydrolytic constant is 9.09. The molecular oxygen and hydroxide ion can be explained to enter into the cavity of macrocyclic ligand stepwisely. This conclusion is in agreement with previous report.

$$Co_2L + O_2 \rightleftharpoons Co_2L(O_2) \quad (1)$$

$$K_{O_2} = \frac{[Co_2L(O_2)]}{[Co_2L]PO_2} = 10^{3.19}$$

$$Co_2L(O_2) \rightleftharpoons Co_2(OH)L(O_2) + H^+ \quad (2)$$

$$K^{OH} = \frac{[Co_2(OH)L(O_2)][H^+]}{[Co_2L(O_2)]} = 10^{-9.09}$$

$$Co_2(OH)L + O_2 \rightleftharpoons Co_2(OH)L(O_2) \quad (3)$$

$$K = \frac{[Co_2(OH)L(O_2)]}{[Co_2L(OH)]PO_2} = 10^{0.9}$$

2.4. Crystal structure of dinuclear cobalt complexes

Figs. 4 and 5 show the ORTEP structure and packing diagram obtained for the homodinuclear cobalt(II) complex. A summary of crystallographic results is given in Table 3. Selected bond lengths and bond angles are given in Table 4. Tables of atomic coordinates and thermal displacement parameters are contained in the Supporting Material.

Two Co(II) ions are located in separate compartments and each of them is six-coordinated, being bonded to three nitrogens donors from a N-(2-aminoethyl)-1,3-propanediamine unit of the macrocycle, one phenolic oxygen and two nitrate oxygens. The geometry around the two cobalt atoms is the same, both being pseudo-octahedral coordination polyhedra with three nitrogen atoms and one oxygen atom O(12) forming the basal
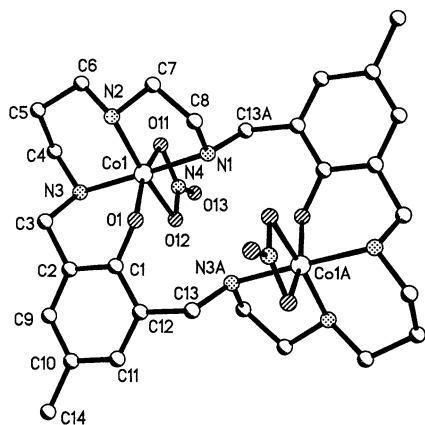
Fig. 4. The ORTEP structure of homonuclear [CO$_2$C$_{28}$H$_{44}$N$_6$O$_2$-(NO$_3$)$_2$]·12(H$_2$O) complex.
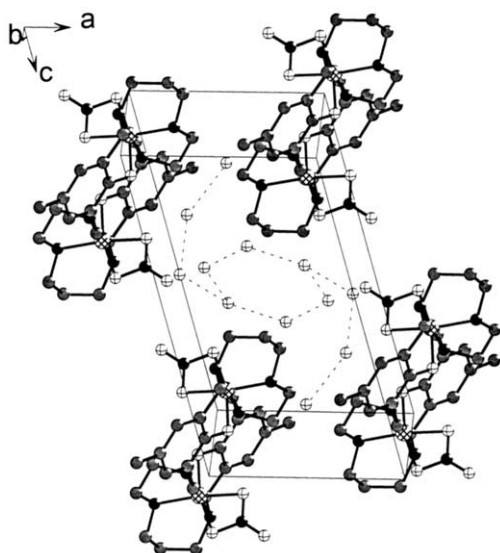
Fig. 5. Cell packing diagram of homonuclear [CO$_2$C$_{28}$H$_{44}$N$_6$O$_2$-(NO$_3$)$_2$]·12(H$_2$O) complexes along c axis.

Table 3
Crystal data and structure refinement details for [Co$_2$C$_{28}$H$_{44}$-N$_6$O$_2$(NO$_3$)$_2$)]·12(H$_2$O)

Molecular formula	[Co$_2$C$_{28}$H$_{44}$N$_6$O$_2$(NO$_3$)$_2$·12(H$_2$O)]
Formula weight	954.76
Crystal color; habit	brown, cubic
Crystal dimensions	0.12 × 0.32 × 0.18 mm
Crystal system	triclinic
Lattice type	primitive
a (Å)	8.3376(5)
b (Å)	9.4501(6)
c (Å)	14.1028(9)
α (°)	73,9100(10)
β (°)	73.4940(10)
γ (°)	87.7310(10)
V (Å^3)	1022.73(11)
Space group	P$\bar{1}$
Z	1
ρ_{calc} (cg cm^{-3})	1.550
$F(000)$	506
θ Range (°)	2.25–26.02
Limiting indices	$6 \geq h \geq -10$; $11 \geq k \geq -10$; $17 \geq l \geq -17$
Absorption coefficient (mm^{-1})	0.899
Temperature (K)	110(2)
λ (Å)	0.71073
p-Factor	0.03
Number of reflections measured	total:5851; unique 3922 (R_{int} = 0.037)
Number of observations	3329 ($I > 2.0\sigma(I)$)
Number of variables	262
R^{a}	0.0618
$R_w{}^{b}$	0.1607
Goodness-of-fit on F^2	1.083
Peak hole in final difference map (e Å^{-3})	0.985; −0.621

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

plane with a mean deviation of 0.091 Å, and oxygen atoms: O(1) and O(11) at the apical position. This molecule has a symmetry center. The macrocyclic ligand serves as the N$_3$O donor to each cobalt ion. Two cobalt atoms, Co(1) lies 0.065 Å above the equatorial plane composed of N(1)N(2)N(3)O(12). The intramolecular Co···Co separation is 5.232(1) Å, which is shorter than the similar dinuclear macrocyclic Cu complexes: [BTBPCu$_2$Br$_2$)]·2(CHCl$_3$)·2(CH$_3$OH) (5.814 Å for the larger ion radii of copper). Compared with other dinuclear macrocyclic copper complexes with or without secondary bridged ligands: [BFBDCu$_2$Cl$_3$]ClO$_4$·0.5H$_2$O (5.34 Å), [BFBDCu$_2$O$_x$](BF$_4$)$_{1.8}$Cl$_{0.2}$·0.5H$_2$O (5.34 Å) or [BPBDCu$_2$](ClO$_4$)$_4$·4DMF (5.4 Å), [11] [BDBPHCu$_2$]-(Cl)(Br) (5.36 Å), [12] Co···Co separation still shorter than all of them, though these ligands have smaller

cavity than BTBP. This results from the existence of two phenol groups in BTBP ligand, which makes the skeleton more rigid than two furan groups in BFBD and two pyridine groups in BPBD. As far as BDBPH is concerned, though it also has two similar phenol groups combined into its macrocyclic skeleton, BTBP has two more carbon atoms in the aliphatic side chain. Thus, BTBP becomes more flexible when the two cobalt atoms enter into the macrocyclic cavity, which can effectively reduce the repulsion of each of the cobalt ions.

The bond lengths between cobalt and three equatorial nitrogen atoms are Co–N(1) 1.973(3) Å, Co–N(2), 1.960(3) and Co–N(2) 1.989(3) Å, respectively. O(l) and O(11) occupied the apical position with distances from the equatorial plane 1.774 and 1.968 Å, respectively. There is only one structural description of [Co$_2$L′′′(NCS)$_2$][ClO$_4$] [13] and [{Co$_2$L$_2$′′(μ-AcO)}$_2$(μ-O$_2$)][ClO$_4$]$_2$·4CH$_3$CN [14] reported by K. Nag et al.

Table 4
Selected bond lengths (Å) and bond angles (°) for $[Co_2C_{28}H_{44}N_6O_2(NO_3)_2)]\cdot 12(H_2O)$

Bond lengths

Co(1)−O(1)	1.909(2)	Co(1)−O(11)	1.920(2)	N(2)−C(6)	1.496(4)
Co(1)−O(12)	1.921(2)	N(2)−C(7)	1.495(4)	N(3)−C(13)	1.487(4)
Co(1)−N(1l)	1.973(3)	N(3)−C(8)	1.498(4)	C(7)−C(8)	1.507(5)
Co(1)−N(2)	1.960(3)	C(1)−C(2)	1.407(4)	C(9)−C(10)	1.386(5)
Co(1)−N(3)	1.989(3)	C(1)−C(12)	1.411(5)	C(11)−C(12)	1.388(5)
O(1)−C(1)	1.347(4)	C(2)−C(9)	1.396(4)	C(12)−C(13)	1.520(4)
O(11)−N(4)	1.346(4)	C(2)−C(3)	1.493(4)	C(10)−C(11)	1.404(5)
O(12)−N(4)	1.314(4)	C(4)−C(5)	1.517(5)	C(10)−C(14)	1.506(5)
O(13)−N(4)	1.226(4)	C(5)−C(6)	1.515(5)	N(1)−C(4)	1.496(4)

Bond angles

O(1)−Co(1)−O(12)	95.86(10)	C(13)−N(3)−C(8)	114.1(3)
O(1)−Co(1)−O(11)	164.64(10)	C(13)−N(3)−Co(l)	118.3(2)
O(11)−Co(1)−O(12)	68.90(10)	C(8)−N(3)−Co(l)	105.99(19)
O(1)−Co(1)−N(2)	93.26(11)	O(1)−C(1)−C(12)	120.9(3)
O(12)−Co(l)−N(2)	170.72(10)	C(2)−C(1)−C(12)	118.3(3)
O(11)−Co(l)−N(2)	101.92(11)	C(9)−C(2)−C(1)	120.7(3)
O(1)−Co(1)−N(l)	93.64(10)	C(9)−C(2)−C(3)	122.8(3)
O(12)−Co(l)−N(l)	90.30(10)	C(1)−C(2)−C(3)	116.5(3)
O(11)−Co(l)−N(l)	88.50(10)	C(10)−C(9)−C(2)	121.5(3)
N(2)−Co(1)−N(1)	90.81(11)	C(9)−C(10)−C(11)	117.4(3)
O(1)−Co(1)−N(3)	84.79(10)	C(9)−C(10)−C(14)	122.2(3)
O(12)−Co(l)−N(3)	92.51(10)	C(11)−C(10)−C(14)	120.4(3)
O(11)−Co(l)−N(3)	93.72(10)	C(12)−C(11)−C(10)	122.5(3)
N(2)−Co(l)−N(3)	86.63(11)	C(11)−C(12)−C(1)	119.6(3)
N(1)−Co(1)−N(3)	176.91(11)	C(11)−C(12)−C(13)	121.0(3)
C(1)−O(1)−Co(1)	117.17(19)	C(1)−C(12)−C(13)	119.4(3)
C(3)−N(1)−C(4)	111.8(2)	N(1)−C(3)−C(2)	110.2(3)
C(3)−N(1)−Co(1)	113.5(2)	N(1)−C(4)−C(5)	113.0(3)
C(4)−N(1)−Co(l)	115.2(2)	N(2)−C(6)−C(5)	113.0(3)
C(7)−N(2)−C(6)	109.2(3)	N(2)−C(7)−C(8)	107.8(3)
C(7)−N(2)−Co(1)	109.3(2)	N(3)−C(8)−C(7)	107.0(3)
C(6)−N(2)−Co(1)	116.1(2)	N(3)−C(13)−C(12)	112.0(3)
O(13)−N(4)−O(11)	124.9(3)	O(12)−N(4)−O(11)	109.5(3)
O(13)−N(4)−O(12)	125.6(3)		

with related unsymmetric tetrakis Schiff bases macrocyclic ligand. In the former structure, the two cobalt centers were located in N_2O_2 cavity and NCS^- ion served as auxiliary ligand to complete five-coordinated polyhedron. When it has been oxygenated, molecular oxygen served as a bridge connected two $[Co_2L''_2(\mu\text{-}AcO)]$ units and completed six-coordination environment. In each complex, phenol oxygen group bridged two cobalt ions and formed a square planar core. But in the title complex, cobalt ions are well separated, which makes the formation of its oxygenated complex possible. When molecular oxygen binds to the title complex, it is supposed that dioxygen atoms would substitute the additional NO_3 ligand and provides the five-coordination site. The most effective way to complete this coordination is form μ-oxo bridge between two cobalt centers. And then, the six-coordination site will be fulfilled with the subsequent bridged hydroxide ion.

Nitrate ion served as an bidentate ligand with bond lengths Co−O(11) and Co−O(12) are 1.920(3), 1.921(3) Å, respectively. The average bond length of Co−N is 1.974 (3) Å, shorter than its analogous dinuclear copper complex (Cu−N(av.) 2.032 Å). The two benzyl rings are drawn to each other due to the coordination of two cobalt atoms by the *NNNO* donor sets of the ligand, with the two phenolic oxygen atoms pointing into the macrocyclic cavity and still keeping antiparallel conformation. All twelve water molecules crystallized in the lattice are connected with hydrogen bonds as in Fig. 5.

2.5. Conclusions

Dicobalt complexes with BTBP of the type $[Co_2L]^{2+}$ and $[Co_2L(OH)]^+$ are efficient receptors of molecular oxygen in aq. solution, giving rise to the formation of $[Co_2O_2L]^{2+}$ and $[Co_2L(OH)O_2]^{2+}$ oxygenated species. In the case of this macrocyclic complex, uncoorperativity is observed in the binding of O_2 in the basic region. The result of thermodynamic calculations showed that the uptake of O_2 and OH^- takes place between two metal ions. The oxygen molecule and hydroxide ion bind with two cobalt center stepwisely via peroxide-bridging coordination mode.

3. Experimental

3.1. Materials

The ligand was synthesized as previously reported. GR grade $Co(NO_3)_2 \cdot 6H_2O$ was obtained from Aldrich Chemical Co. The Co^{2+} stock solution for the potentiometric studies was reagent grade nitrate salt solutions prepared with doubly distilled water and standardized with cationic exchange techniques (Dowex 50W X8 cation exchange resin 20–50 mesh, hydrogen form). 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 acid phthalate with phenolphthalein as an indicator. The extent of carbonated accumulation ($\leq 0.5\%$) was checked periodically by titration with a standard HCl solution. Mass spectra (FAB^+) were obtained with a VG analytical 70s high-resolution double focusing magnetic sector spectrometer. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

3.2. Potentiometric equipment

A Corning 250 digital pH meter, fitted with Fisher full-range blue-glass and a Fisher calomel reference electrode, 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.

3.3. Potentiometric determinations

All pH calibrations were performed with standardized KOH in aq. solutions to measure hydrogen ion concentrations directly ($pH = -\log[H]^+$). The ionic strength of the medium was adjusted to 0.100 M with the addition of KCl solution. Titrations of the ligand in the absence or presence of metal ions in aq. 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. The oxygenation constant was determined under 1 atm purified oxygen 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 H_8L^{6+} plus other components (KCl solution, metal solution) was carried out in experimental runs. The concentrations of the sample solutions were 1×10^{-3} M for ligand. The titrations of $Co(II)–H_8L^{6+}$ in 1:1 and 2:1 ratios, were carried out separately to investigate the mononuclear and homodinuclear complexes. The pH range for accurate measurements was considered to be 2–12. The pK_w for the aq. system, defined as $-\log([H^+][OH^-])$ at the ionic strength employed, was found to be 13.78 [15].

3.4. Computations

Protonation constants and stability constants from the direct titrations were calculated from the potentiometric data with the program BEST developed by the Martell group. Species distribution diagrams were computed from the measured equilibrium constants with SPE and plotted with SPEPLOT [15].

3.5. Synthesis of cobalt(II) complexes

$H_2L \cdot 6HBr \cdot 2H_2O$ (0.051 g, 0.05 mmol) was dissolved into 10 ml water and neutralized with 0.1 M KOH till pH 6. Then 2 equiv. $Co(ClO_4)_2 \cdot 6H_2O$ (0.037 g, 0.1 mmol) and KNO_3 (0.056 g, 0.1 mmol) were added into above solution, and were stirred overnight at r.t. The dark brown solution was filtered and precipitates were discarded. A brown solution was evaporated slowly at r.t. to grow dark brown cubic crystals suitable for X-ray diffraction. Dark brown crystalline products were filtered and dried under vacuum. Yield: 0.011 g, 23.27%. m.p. 225 °C. *Anal.* Calc. for $[Co_2C_{28}H_{44}N_6O_2(NO_3)_2] \cdot 12(H_2O)$. C, 35.90; H, 7.10; N, 11.96; Found: C, 36.11; H, 7.20; N, 11.36%. FAB MS: $[(Co_2C_{28}H_{44}N_6O_2)(NO_3)_2]^+$ m/z 738, $[Co_2C_{28}H_{44}N_6O_2$ m/z 614, $[CoC_{28}H_{44}N_6O_2+H]^+$ m/z 559.

3.6. X-ray structure analysis

Crystals of $[Co_2C_{28}H_{44}N_6O_2(NO_3)_2] \cdot 12(H_2O)$ were mounted on a glass fiber at r.t. Preliminary examination and data collection were performed in a Siemens P4 diffractometer (Mo Kα radiation) at 110(2) K. Cell parameters were calculated from the least-squares fits of 25 high-angle reflections ($2\theta > 26.02°$). Three standards collected every 97 reflections, showed no significant trends. Lorentz and polarization corrections were applied to 3922 ($R_{int} = 0.0370$) reflections for $[Co_2C_{28}H_{44}N_6O_2(CO_3)_2] \cdot 12(H_2O)$. Semi-empirical absorption corrections were applied. A total of 5851 unique observed reflections for $[Co_2C_{28}H_{44}N_6O_2(CO_3)_2] \cdot 12(H_2O)$ were used in further calculations. The structures were solved by direct methods (SHELXS-97) [16]. Full-matrix least-squares anisotropic refinements for all non-hydrogen atoms yielded $R = 0.0618$ and $R_w = 0.1607$ [17]. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the heavy atoms to which they were connected. Crystal data and additional details regarding data collection and refinement are listed in Table 3.

Acknowledgements

References

[1] A.E. Martell, D.T. Sawyer (Eds.),Oxygen Complexes and Oxygen Activation by Transition Metals, Plenum Press, New York, 1988.

[2] L.I. Simandi (Ed.),Activation and Homogeneous Catalytic Oxidation, Elsevier, Amsterdam, 1991.

[3] A.E. Martell, Acc. Chem. Rev. 15 (1982) 155.

[4] A.E. Martell, R.J. Motekaitis, D. Chen, I. Murase, Pure Appl. Chem. 65 (1993) 959.

[5] B. Bosnich, Inorg. Chem. 38 (1999) 2554.

[6] D.Y. Kong, A.E. Martell, R.J. Motekaitis, Supramol. Chem. 13 (2001) 447.

[7] R.J. Motekaitis, A.E. Martell, J.M. Lehn, E. Watanabe, Inorg. Chem. 21 (1982) 4253.

[8] D.Y. Kong, J.G. Mao, A.E. Martell, A. Clearfield, unpublished work.

[9] D.Y. Kong, J.H. Reibenspies, A.E. Martell, R.J. Motekaitis, Inorg. Chim. Acta 324 (2001) 35.

[10] (a) A. Bebcini, A. Bianchi, C. Giorgi, P. Paoletti, B. Valtancoli, N. Ceccanti, R. Pardini, Polyhedron 19 (2000) 2441;
(b) N. Ceccanti, R. Pardini, F. Secco, M.R. Tiné, M. Venturini, A. Bianchi, P. Paoletti, B. Valtancoli, Polyhedron 19 (2000) 2447.

[11] Q. Lu, R.L. Carroll, J.H. Reibenspies, A.E. Martell, A. Clearfield, J. Mol. Struct. 470 (1998) 121.

[12] D.Y. Kong, J.H. Reibenspies, A.E. Martell, R.J. Motekaitis, Inorg. Chim. Acta 317 (2001) 243.

[13] H. Furuttachi, H. Ōkawa, Inorg. Chem. 36 (1997) 3911.

[14] H. Furuttachi, S. Fujinami, M. Suzuki, H. Ōkawa, Chem. Lett. 8 (1998) 779.

[15] A.E. Martell, R.J. Motekaitis, The Determination and Use of Stability Constants, 2nd ed., VCH Publishers, New York, 1992.

[16] G. Sheldrick, SHELXS-86 Program for Crystal Structure Solution, Universität Göttingen, Göttingen, Germany, 1986.

[17] G. Sheldrick, SHELXL-97 Program for Crystal Structure Refinement, Universität Göttingen, Göttingen, Germany, 1997.