Synthesis and Structural Characterization of Five- and Six-Coordinate Cobalt(II) Complexes of Tripodal Liand, Tris-(2-benzimidazolylmethyl)amine

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The various cobalt(II) complexes were synthesized and characterized using tris-(2-benzimidazolylmethyl)amine (ntb) as a ligand where the ntb plays as a tripodal tetradentate ligand to form complexes with a trigonal pyramidal geometry. The complexes have 5 and 6 coordinate cobalt(II) ions depending on the additional ligand used. In each complex the additional ligand, chloride anion, or acetate anion occupies the "open" site trans to the apical tertiary nitrogen atom of ntb ligand. Complex **1,** [Co(II)(ntb)Cl]Cl has a trigonal bipyramidal geometry. This geometry was easily constructed using ntb as a tetradentate ligand and chloride as a monodentate ligand. The complex is isostructural to the corresponding manganese(II) complex. Crystal data are as follows: [Co(II)(ntb)Cl]Cl · MeOH, **1** . triclinic space group $P\bar{1}$; a=13.524(2) Å, b=14.037(2) Å, c=17.275(1) Å; α= 78.798(9), β=84. 159(8)°, γ=65.504(9)°; V=2929.6(6) Å^3; Z=4; R1=0.0715, wR2 =0.1461 for reflections of I> 2σ(I). Six coordinate complex **2** [Co(ntb)(OAc)](OAc) was synthesized using ntb as a tetradentate ligand and acetate as a bidentate chelating ligand.

Introduction

The metal complexes of tripod-like ligands with a variety of ligating groups have been widely investigated, since they may serve as model compounds for the active site of metalloproteins[1] in addition to their special chemical, physical, structural properties.[2] There has been a considerable amount of research conducted on the cobalt-substituted metalloproteins.[3] The primary reason for the substitution, for example cobalt for zinc, is the paramagnetism of cobalt and its sensitivity to changes in its coordination geometry that appear in its visible absorption spectra.

Geometry preference of the tripodal ligand, tris-(2-benzimidazolylmethyl)amine(ntb) is marginal. Depending on metal ions and additional ligands used, various geometries have been observed. Both trigonal bipyramidal and octahedral geometries were observed in manganese[4] and zinc complexes.[5] However, iron complexes preferred octahedral geometry.[6]

To date, although many tripodal metal complexes have been reported, it appears that there are only a few structurally characterized tripodal cobalt(II) complexes.[4d] In this study, we synthesized and characterized various cobalt(II) complexes of tripod-like ligand, ntb. These complexes may serve as model complexes of the cobalt(II)-substituted metalloproteins where the imidazole portion of the ligand serves as the model for the histidine residue and the benzene portion of the ligand for the hydrophobic environment. They may also give information on the flexibility of ntb ligand and the geometry preference of the cobalt(II) ion.

Experimental Section

Materials. The following were used as received with no further purification: ntb(Aldrich), cobalt chloride hexahydrate(Yakuri), cobalt acetate tetrahydrate (Aldrich), and methanol (Carlo Erba).

Elemental Analysis. C, H, N and Co determinations were performed by the elemental analysis laboratory of the Korean Institute of Basic Science.

IR spectra. Infrared spectra were recorded as KBr pellets in the range 4000-400 cm^{-1} on a Bio-Rad FT-IR spectrometer.

Absorption spectra. Absorption spectra were obtained in methanol on a Perkin Elmer Lambda 7 UV spectrometer.

Mass spectra. Positive ion FAB mass spectra were obtained using a JEOL HX110A/HX110A Tandem Mass Spectrometer in 3-nitrobenzyl alcohol matrix.

Magnetic Susceptibility Measurements. Room temperature magnetic susceptibilities were made on well ground solid samples using an Evans balance. The measurements were calibrated using $Hg[Co(SCN)_4]$ standard.

Synthesis. [Co(II)(ntb)Cl]Cl, **1.** 0.407 g (1 mmol) of ntb was added to 20 mL of methanol in a 100 mL Erlenmeyer flask. When 0.235 g (1 mmol) of cobalt(II) chloride hexahydrate was dissolved in 5 mL of methanol in 50 mL flask, the solution was purple. The cobalt chloride solution was added to the ligand solution over a one-minute period. The mixture solution was stirred for five minutes. After slow evaporation of the solution for two days, pale purple rectangular crystals suitable for crystallographic study were obtained (0.405 g, 68% yield). Anal. Calcd for $[Co(II)(ntb)Cl]Cl \cdot H_2O(CoC_{24}H_{27}N_7O_3Cl_2)$: C, 48.75; H, 4.60; N, 16.58; Co, 9.97%. Found: C, 48.85; H. 4.53; N, 16.27; Co, 9.72%. FAB (Fast Atom Bombardment) mass spectrum: m/z of $[Co(ntb)Cl]^+$, 500.9; $[Co(ntb)-H]^+$, 465.0. μ_{eff}: 4.62 BM. λ_{max}(ε), 554 nm (290 L/mol · cm); 591 nm(272 L/mol · cm).

[Co(ntb)(OAc)](OAc) H_2O, **2.** Complex was prepared similarly to that for [Co(II)(ntb)Cl]Cl, **1.** 0.407 g (1 mmol) of ntb was dissolved in 20 mL of methanol and 0.249 g (1 mmol) of cobalt(II) acetate tetrahydrate was dissolved using 10 mL of methanol in another flask. Two solutions were

mixed and stirred. The mixture turned to a pink colored turbid solution. After one hour of stirring the solution was filtered. After slow evaporation of the filtrate solution for two days, pale pink colored needles were obtained (0.29 g, 45% yield). Anal. Calcd for [Co(ntb)(OAc)](OAc) · H_2O (CoC_{28}-$H_{33}N_7O_7$): C, 52.67; H, 5.21; N, 15.35; Co, 9.23%. Found: C, 52.35; H. 5.16; N, 15.35; Co, 9.78%. FAB mass spectrum: m/z of $[Co(ntb)(OAc)]^+$, 525.2; m/z of $[Co(ntb)-H]^+$, 465.1 IR: 1575 cm^{-1} and 1545 cm^{-1} (shoulder), 1400 cm^{-1} for two acetate ions. μ_{eff}: 4.65 BM. λ_{max} (ε), 529 nm (214 L/mol · cm); 590 nm (174 L/mol · cm).

Crystallographic Data Collections and Refinements of Structures. Crystal **1** loses its structural solvents within a minute. Crystal **1** was mounted in the glass capillary with mother liquor to prevent the loss of the structural solvents during data collections. Preliminary examinations and data collections were performed with Mo Kα radiation (λ=0.71069 Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and orientation matrixes for data collections were obtained from least-squares refinement, using the setting angles of 25 reflections. Data were collected at a room temperature using ω scan technique. Three standard reflections were monitored every hour and no intensity variations were monitored. Lorentz and polarization corrections were applied to the data. No absorption corrections were applied to the data. The structure was solved by direct method using SHELXS-86[7a] and refined by full-matrix least-squares with SHELXL-93.[7b] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were ridden on a geometrically ideal position with 1.2 times isotropic temperature factors of the attached non-hydrogen atoms.

Details on crystals and intensity data are given in Table 1.

Results and Discussion

Five Coordinate Cobalt(II) Complex. [Co(II)(ntb)Cl]Cl, **1** could be synthesized using cobalt(II) chloride as a metal source and ntb as a neutral tripodal tetradentate ligand, Crystal structure showed two crystallographically independent but chemically identical molecules. An ORTEP drawing of one of these molecules (complex **1)** is shown in Figure 1. The neutral tripodal tetradentate ligand forms trigonal pyramidal geometry with the cobalt(II) ion and the monodentate chloride anion occupies the remaining "open" axial position to finish the trigonal bipyramidal geometry. Another chloride anion exists as a counter ion. The charge balance of the crystal structure and the magnetic susceptibility measurement suggest that the oxidation state of cobalt ion is +2. FAB mass spectrum of complex **1** gave a peak at 500.9 of m/z for $[Co(ntb)Cl]^+$. The average bond distance between the cobalt ion and the apical nitrogen atom (N1) is 2.396 Å (2.384(6) Å and 2.407(5) Å) and is about 0.36 Å longer than those between the cobalt ion and the trigonal basal nitrogen atoms (2.029(6) Å-2.055(6) Å, avg.= 2.040Å) (Table 2). This significant elongation is also observed in other cobalt complexes of tripodal tetradentate ligand with a benzimidazolylmethyl group.[4d] Similar elongations are also observed in manganese, zinc, and iron complexes of analogous ligands.[4-6] The average bond angle (N_A-Co-N_B) of apical nitrogen atom (N_A), cobalt ion, and trigonal basal nitrogen atom (N_B) is 75.4°. The cobalt ion is 0.51 Å above the trigonal basal plane. The fifth ligand chloride anion is located trans to the apical nitrogen, and the bond angle N_A-CO-Cl is 178.5°. An isostructural manganese (II) complex has recently been known (Table 2).[4e] The average bond distance of the cobalt complex is about 0.11Å shorter than that of the corresponding manganese complex. This difference in the bond distance is due to the difference of the metal size. The ionic radius of a high spin five coordinate d^7 cobalt ion is 0.67 Å whereas of a high spin five coordinate d^5 manganese ion is 0.75 Å.[8]

Six Coordinate Cobalt(II) Complex. [Co(ntb)(OAC)](OAC), **2** was synthesized similarly to that for complex **1** using cobalt(II) acetate as a metal source. Magnetic susceptibility measurement suggests that complex **2** also has a high spin cobalt(II) ion. IR spectrum of complex **2** is very similar to that of complex **1** except for additional broad acetate peaks at 1575 cm^{-1}, 1545 cm^{-1} (shoulder) and 1400 c m^{-1}. FAB mass spectrum of complex **2** shows m/z of 525.5

Table 1. Crystal data and structure refinement for [Co(ntb)Cl]Cl · MeOH, **1**

Empirical formula	$CoC_{26}H_{29}N_7O_2Cl_2$
Formula weight	601.39
Temperature	293(2) K
Wavelength	0.71069
Space group	$P\bar{1}$
Unit cell dimensions	a=13.524(2) Å alpha=78.798(9)°
	b=14.037(2) Å beta=84.159(8)°
	c=17.275(1) Å gamma=65.504(9)°
Volume	2926.6(6) $Å^3$
Z	4
Crystal size	0.20 x 0.40 x 0.70 mm
θ range for data collection	1.20 to 22.48°
Independent reflections	7644
Goodness-of-fit on F^2	1.148
Final R indices [I>2σ(I)]	R1=0.0715, wR2=0.1461
R indices (all data)	R1=0.1072, wR2=0.1602
Largest cliff. peak and hole	0.324 and – 0.267 e. $Å^{-3}$

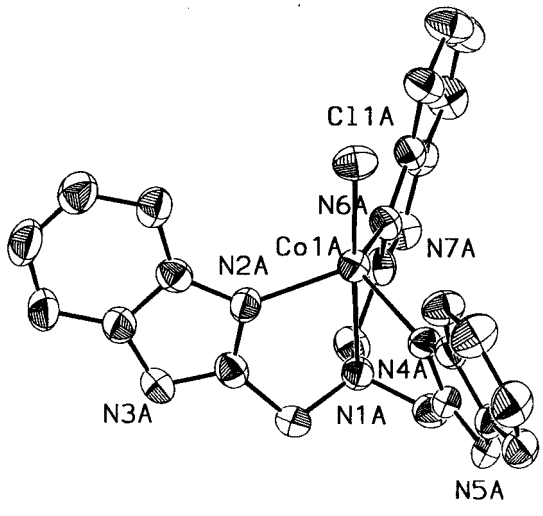

Figure 1. An ORTEP drawing of complex **1,** $[Co(II)(ntb)Cl]^+$.

Table 2. Comparison of the bond lengths **[Å]** and angles [°] for [Co(ntb)Cl]Cl · MeOH, **1** and [Mn(ntb)Cl]Cl[4e]

Co(1)-N(1)	2.384(6)	2.407(5)	Mn(1)-N(1)	2.519(8)	2.501(9)
Co(1)-N(2)	2.039(6)	2.051(6)	Mn(1)-N(2)	2.137(8)	2.169(10)
Co(1)-N(4)	2.055(6)	2.030(6)	Mn(1)-N(4)	2.149(9)	2.162(9)
Co(1)-N(6)	2.029(6)	2.033(5)	Mn(1)-N(6)	2.166(8)	2.154(10)
Co(1)-Cl(1)	2.288(2)	2.296(2)	Mn(1)-Cl(1)	2.363(3)	2.357(4)
N(2)-Co(1)-N(1)	75.8(2)	75.8(2)	N(2)-Mn(1)-N(1)	72.7(3)	72.9(3)
N(4)-Co(1)-N(1)	74.8(2)	75.7(2)	N(4)-Mn(1)-N(1)	73.1(3)	73.6(3)
N(6)-Co(1)-N(1)	75.5(2)	74.9(2)	N(6)-Mn(1)-N(1)	72.6(3)	73.6(3)
Cl(1)-Co(1)-N(1)	177.9(2)	179.1(2)	N(4)-Mn(1)-N(2)	117.9(3)	117.0(4)
N(2)-Co(1)-N(4)	110.5(2)	115.4(2)	N(6)-Mn(1)-N(2)	111.4(3)	107.0(4)
N(6)-Co(1)-N(2)	112.7(2)	109.1(2)	N(6)-Mn(1)-N(4)	105.4(3)	112.3(3)
N(2)-Co(1)-Cl(1)	106.2(2)	103.5(2)	N(2)-Mn(1)-Cl(1)	106.5(3)	103.9(3)
N(6)-Co(1)-N(4)	118.2(2)	117.2(2)	N(4)-Mn(1)-Cl(1)	109.4(3)	105.2(3)
N(4)-Co(1)-Cl(1)	103.9(2)	104.1(2)	N(6)-Mn(1)-Cl(1)	105.5(3)	111.0(3)
N(6)-Co(1)-Cl(1)	104.0(2)	106.0(2)	Cl(1)-Mn(1)-N(1)	177.3(2)	175.1(3)
disp. [a]	0.516(4)	0.512(4)		0.635(5)	0.619(6)

[a] displacement of metal ions from N2, N4 and N6 atom plane

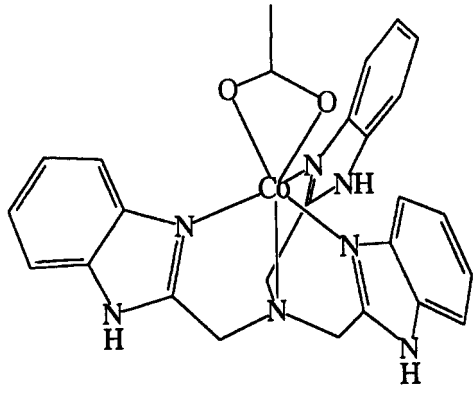

Figure 2. Proposed structure for complex **2,** [Co(II)(ntb)(OAc)]$^+$.

for [Co(ntb)(OAc)]$^+$.

Recently the same tripodal ligand ntb manganese complex with a chelating bidentate acetate group, [Mn(II)(ntb)(OAc)]Cl, was reported.[4e] ntb formed the trigonal pyramidal geometry with manganese ion in the complex, and the remaining "open" axial site of the complex was occupied by a chelating bidentate acetate anion. The complex has a six-coordinate manganese geometry. The comparison of the IR spectra of both cobalt(II) and manganese complexes, the separations of acetate peaks (175 cm^{-1} and 145 cm^{-1} for complex **2** ; 150 cm^{-1} for [Mn(II)(ntb)(OAc)]$^+$) and the mass spectra of the cobalt complexes suggest that both metal complexes are isostructural to each other except the counter ions. The manganese complex binds the acetate ion at the "open" axial position as a chelating bidentate ligand. Presumably, the complex **2** binds the acetate ion at the same location, as shown in Figure **2.**

Geometry preference of the tripodal ligand, ntb is marginal. The cobalt(II) complex could have various geometries depending on the location of additional ligands. In the presence of chloride anions the complex has trigonal bipyramidal geometry. In the presence of a bidentate acetate anion the complex has trigonal pyramidal partial geometry with additional ligand coordinated at the trans "open" site. However, in the presence of isothiothianate anion the complex has distorted octahedral geometry.[4d] Similar behavior has been observed in the corresponding manganese complexes.[4e] Iron(III) complexes, however, preferred distorted octahedral geometry.[7] Dinuclear iron(III) complex, $[Fe(III)_2(ntb)_2OCl_2]^{2+}$ had distorted octahedral iron centers. The complexes of tripodal ligand, ntb could have various geometries depending on the metal used and the additional ligands coordinated.

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Supporting Information Available. Tables giving atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for non-hydrogen atoms and atomic coordinates for hydrogen atoms of **1** (12 pages) and an ORTEP drawing with complete atomic numbering of **1** is available. Supplementary materials are available from M. S. Lah.

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Selective Acyl and Alkylation of Monobenzoyl *p-tert*- Buty1calix[4]arene

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Several calixarene derivatives of 5,11,l7,23-tetra- *tert* -butyl-25-(3,5-dinitrobenzoyloxy)-26,27,28-trihydroxycalix [4]arene **2** were synthesized by the reaction of **2** with several acyl and alkylating agents in the presence of base such as pyridine and K_2CO_3 in THF. Acylation of monobenzoylated *p-tert*- butylcalix[4]arene **2** yielded their corresponding 1,3-diacylated calix[4]arenes **3a-3g.** On the other hand, alkylation of **2** produced a variety calix[4]arene derivatives such as 1,2- and l,3-disubstituted calix[4]arenes **4a-4c, 4e-4f,** or 1,2,4-trisubstituted calix[4]arene **4d.** l,2-Disubstituted calix[4]arenes are chiral. All derivatives exist as a cone conformation based on NMR studies.

Introduction

Gutsche and his coworkers[1,2] discovered the selective esterification of *p-tert*- butylcalix[4]arene by the reaction of 3,5-dinitrobenzoyl chloride with calixarene in the presence of base. They reported that under the carefully controlled reaction conditions one monoester, two diesters (1,2- and 1,3-disubstituted) and one triester could be prepared selectively. By taking advantage of the reaction of the preparation of monoester, we recently published the synthetic procedure[3] for the monoalkyl calix[4]arene and the selective acylation[4] of calix[4]arene. To further extend the chemistry of selective functionalization of calix[4]arene we utilized the function of bulky group such as 3,5-dinitrobenzoyl at the lower rim and *p-tert*- butyl group at the upper rim of calixarene for the selective introduction of the different second and third, and possibly the fourth substituents at the lower rim of calixarene.

For the introduction of second substituents, 5,11,17,23-tetra- *tert* -butyl-25-(3,5-dinitrobenzoyloxy)-26,27,28-trihydroxycalix[4]arene("25-monoester **2** ") was treated with several different acyl as well as alkyl halides in the presence of base, which produced ester and ether substituents in one calixarene. For the reaction of acyl halides all 1,3-disubstituted calixarenes were obtained as expected, but a variety of products such as 1,2-(chiral), 1,3-disubstituted and 1,2,4-trisubstituted calix[4]arenes were obtained for the reaction of alkyl halides.

Results and Discussion

Acylation of Monobenzoylated Calix[4]arene 2. Since it is not possible to introduces[5-7] directly two different acyl groups between the four hydroxy moities at the lower