

Synthesis and Crystal Structure of 13-Membered Tetraaza Macrocyclic Cobalt(III) Complex with Azido Ligand

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Azido 리간드가 포함된 13변 테트라아자 거대고리 코발트(III) 錯物の 合成 및 結晶構造

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Abstract

The complex *cis*-[Co(13-aneN₄)(N₃)₂]Cl·H₂O (**1**) (13-aneN₄ = 1,4,7,10-tetraazacyclotridecane) has been synthesized and structurally characterized by X-ray crystallography. It crystallizes in the orthorhombic system *Pbca*, *a* = 7.8282(4) Å, *b* = 14.3197(7) Å, *c* = 29.9021(15) Å, *V* = 3351.9(3) Å³, *Z* = 8. The cobalt(III) ion in **1** is coordinated to four nitrogen atoms from the macrocycle and two azide ligands of *cis* position in a distorted octahedral environment, which forms the 1D polymer through hydrogen bonding contacts involving the cation, chloride anion and solvent water molecules.

要 約

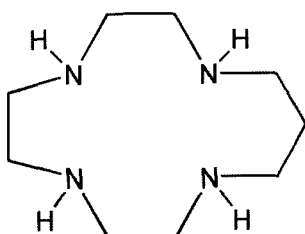
cis-[Co(13-aneN₄)(N₃)₂]Cl·H₂O (**1**) (13-aneN₄ = 1,4,7,10-tetraazacyclotridecane) 錯物を 合成하고 構造를 糾明하였다. 이 錯物は 單斜晶系, 空間群 *Pbca*, *a* = 7.8282(4) Å, *b* = 14.3197(7) Å, *c* = 29.9021(15) Å, *V* = 3351.9(3) Å³, *Z* = 8로 決定化 되었다. 錯物 **1**의 코발트(III) 이온은 巨대고리 리간드의 4개의 窒素原子와 시스 위치에 2개의 azide 리간드가 結合한 若干 일그러진 八面體 構造를 갖는데, 錯物の 양이온, 鹽素 음이온 및 물分子를 통하여 1차원의 水素結合을 形成한다.

1. Introduction

Recently, the cyclam (1,4,8,11-tetraazacyclotetradecane) and modified cyclam cobalt(III) complexes have been synthesized and structurally characterized by spectroscopy and X-ray crystallography.¹⁻⁸⁾ For example, *trans*-[Co(cyclam)Cl₂]Cl·4H₂O·0.47HCl⁵⁾ and [Co(H₂ddta)Cl₂] (ClO₄)₃·2H₂O (ddta=6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)⁶⁾ exhibit a low-spin octahedral geometry with four nitrogen atoms of the macro-

cycle and two chloride ligands of *trans* position. Also, in a hexaazamacrocyclic cobalt(III) complex [Co(ddta)](ClO₄)₃⁶⁾ the cobalt(III) ion has a distorted octahedral geometry with four secondary amines of the macrocycle and two pendant amines at the axial position. The structures of cobalt(III) complexes containing azide ligands are complicated by the presence of several binding modes for the azido ligands. In a previous paper, the complex *trans*-[Co(dttd)(N₃)₂]N₃·2H₂O (dttd=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,18},0^{7,12}]docosane)⁸⁾

reveals a distorted octahedron with four nitrogen atoms of the macrobicycle and two azido ligands of *trans*-position. However, the structure of [Co(tren)(N₃)₂]ClO₄ (tren = 2,2',2''-triaminotriethylamine)⁹ shows a distorted octahedral geometry and *cis* arrangement of the two single coordinated azido ligands. To further investigate the different molecular geometry, we report the synthesis and crystal structure of cobalt(II) complex, *cis*-[Co(tatd)(N₃)₂]Cl·H₂O (**1**) (13-aneN₄=1,4,7,10-tetraazacyclotridecane).

13-aneN₄

2. Experimental

Materials and Physical Measurements. All chemicals and solvents used in the synthesis were of reagent-grade and used without further purification. The 1,4,7,10-tetraazacyclotridecane (13-aneN₄) and *trans*-[Co(13-aneN₄)Cl₂]Cl were prepared according to the literature method.¹⁰ IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analysis (C, H, N) were performed on a Perkin Elmer CHN-2400 analyzer.

Synthesis of *cis*-[Co(13-aneN₄)(N₃)₂]·H₂O (**1**).

To a MeOH solution (20 mL) of *trans*-[Co(13-aneN₄)Cl₂]Cl (176 mg, 0.5 mmol) was added NaN₃ (33 mg, 0.5 mmol). The mixture was heated to reflux for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until the violet crystals formed. The

Table 1. Crystal data and structure refinement for 1

Empirical formula	C ₉ H ₂₄ N ₁₀ ClCoO
Formula weight	382.76
Temperature	293(2) K
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	<i>a</i> =7.8282(4) Å <i>b</i> =14.3197(7) Å <i>c</i> =29.9021(15) Å
Volume	3351.9(3) Å ³
<i>Z</i>	8
Density (calculated)	1.517 Mg/m ³
Absorption coefficient	1.202 mm ⁻¹
Diffractometer	CCD area detector/ω-2θ
Radiation/wavelength	Mo Kα (graphite monochrom.)/0.71073 Å
<i>F</i> (000)	1600
Crystal size	0.14×0.13×0.05 mm ³
θ range for data collection	1.36 to 28.40°
Index ranges	-10≤ <i>h</i> ≤10, -17≤ <i>k</i> ≤19, -39≤ <i>l</i> ≤28
Reflection collected/unique	34608/4201 (<i>R</i> _{int} =0.2001)
Absorption correction	<i>T</i> _{max} =0.9417 and <i>T</i> _{min} =0.0019
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4201/0/194
Goodness-of-fit on <i>F</i> ²	1.045
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ ^a =0.1503, <i>wR</i> ₂ ^b =0.3866
<i>R</i> indices (all data)	<i>R</i> ₁ ^a =0.2799, <i>wR</i> ₂ ^b =0.4347
Largest diff. peak and hole	3.026 and -1.489 eÅ ⁻³

^a*R*₁=Σ||*F*_o|-|*F*_c||/Σ|*F*_o|.

^b*wR*₂=[Σ[w(*F*_o²-*F*_c²)²/Σ[w(*F*_o²)]]^{1/2}.

product was filtered and recrystallized from a hot H₂O/MeOH (1:1 v/v, 20 mL) mixture. Found: C, 28.12; H, 6.43; N, 36.71. Calc. for C₉H₂₄N₁₀ClCoO: C, 28.24; H, 6.32; N, 36.60%. IR (KBr, cm⁻¹): 3184 (NH), 3174 (NH), 2062 (N₃), 2020 (N₃).

X-ray Crystallography. A red crystal was mounted on a CCD area diffractometer. Intensities were collected with a graphite-monochromated Mo K α radiation ($\lambda=0.71073$ Å), using the $\omega/2\theta$ scan technique at 293 K. Accurate cell parameters and an orientation matrix were determined by the least-squares fit of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was applied by ψ -scan.¹¹ The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. The structure was solved by direct methods¹² and the least-squares refinements of the structure were performed by the program SHELXL97.¹³ All atoms except for all hydrogen atoms were refined aniso-

tropically. Hydrogen atoms were placed in calculated positions allowing to ride on their parent C atoms with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C or N})$. The rather higher R_1 and wR_2 values may be attributed mainly to the bad quality of the sample compound. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and Discussion

An ORTEP drawing¹⁴ of *cis*-[Co(13-aneN₄)(N₃)₂]Cl·H₂O (**1**) with the atomic numbering scheme is shown in Fig. 1. The selected bond lengths and angles are listed in Table 3. The structure of **1** consists of isolated [Co(13-aneN₄)(N₃)₂]⁺ cation with a distorted octahedral geometry and *cis* arrangement of the two single coordinated azido ligands, a chloride counter anion and one water molecule. The four Co-N distances of the macrocyclic ligand [1.972(11), 1.920(11), 1.936(11), 1.966(11) Å] are similar to those of the two Co-N(azido) [1.936(13), 1.962(13) Å]. The average Co-N (macrocycle) bond distance of 1.949(6) Å is smaller than those observed in *trans*-[Co(cyclam)Cl₂]Cl·4H₂O·0.47HCl [1.974(2) and 1.981(2) Å]⁵ and *cis*-[Co(cyclam)(en)]Cl₃·3H₂O [1.996(2) Å].¹ This fact may be attributed the decrease of the ring cavity size by 13-membered macrocycle (13-aneN₄) compared to 14-

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Co	1520(2)	5404(1)	1127(1)	57(1)
Cl(1)	595(3)	2472(2)	1901(1)	38(1)
N(1)	3977(14)	5668(9)	1200(4)	70(1)
N(2)	1699(15)	4700(7)	1672(4)	63(3)
N(3)	832(14)	6406(7)	1523(4)	63(3)
N(4)	1177(15)	6299(7)	637(4)	71(4)
N(5)	2163(15)	4316(9)	781(4)	73(4)
N(6)	1802(15)	4168(9)	389(6)	73(3)
N(7)	1590(20)	3942(14)	17(5)	130(7)
N(8)	910(17)	5078(9)	1091(4)	80(4)
N(9)	1141(16)	4326(10)	980(5)	79(4)
N(10)	1917(19)	3632(10)	849(6)	110(5)
Ow(1)	6843(16)	3439(10)	2128(5)	129(5)
C(1)	4699(18)	4945(11)	1506(5)	78(5)
C(2)	3480(20)	4757(13)	1826(6)	95(5)
C(3)	460(30)	5053(14)	1981(7)	116(7)
C(4)	60(20)	6023(11)	1922(5)	84(5)
C(5)	300(20)	7088(12)	1277(6)	90(5)
C(6)	680(20)	7168(12)	833(8)	116(7)
C(7)	2540(20)	6412(12)	287(6)	94(5)
C(8)	4390(20)	6562(13)	463(7)	111(6)
C(9)	4920(20)	5767(15)	776(7)	111(6)

^a*U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

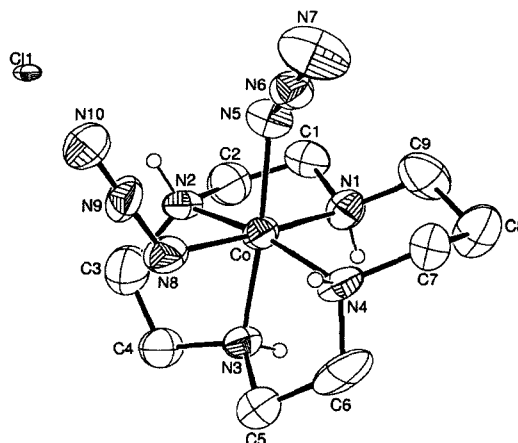


Fig. 1. An ORTEP drawing of **1 with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability. The hydrogen atoms and water molecule are omitted for clarity.**

Table 3. Selected bond distances (Å) and angles (°) for 1

Bond lengths			
Co-N(1)	1.972(11)	Co-N(2)	1.920(11)
Co-N(3)	1.936(11)	Co-N(4)	1.966(11)
Co-N(5)	1.936(13)	Co-N(8)	1.962(13)
N(5)-N(6)	1.223(17)	N(6)-N(7)	1.171(17)
N(8)-N(9)	1.192(17)	N(9)-N(10)	1.140(16)
Bond angles			
N(1)-Co-N(2)	86.3(5)	N(1)-Co-N(3)	93.6(5)
N(1)-Co-N(4)	95.2(5)	N(2)-Co-N(3)	83.7(5)
N(2)-Co-N(4)	169.9(5)	N(3)-Co-N(4)	86.2(5)
N(5)-Co-N(1)	87.7(5)	N(5)-Co-N(2)	90.7(5)
N(5)-Co-N(3)	174.2(5)	N(5)-Co-N(4)	99.3(5)
N(5)-Co-N(8)	91.8(5)	N(8)-Co-N(1)	175.9(5)
N(8)-Co-N(2)	89.6(5)	N(8)-Co-N(3)	86.6(5)
N(8)-Co-N(4)	88.9(5)	Co-N(5)-N(6)	126.2(10)
Co-N(8)-N(9)	123.3(11)	N(5)-N(6)-N(7)	172.2(15)
N(8)-N(9)-N(10)	175.6(18)		

membered cyclam. The average Co-N (azido) distance of 1.949(9) Å is similar to those found in azido cobalt(III) complexes *mer*-[Co(dmp)₃(N₃)₃] [dmp=3,4-dimethylpyridine; 1.931(4) to 1.959(4) Å]¹⁵ and *cis*-[Co(tren)₃(N₃)₂]ClO₄ [tren = 2,2',2''-triiminotriethylamine; 1.964(3) and 1.946(3) Å]⁹ in which the cobalt(III) ion adopts a distorted octahedral geometry. The basal plane contains three nitrogen atoms of the macrocycle and one nitrogen atom of the azido ligand with a slightly distortion [deviation N(1) -0.085(6), N(2) 0.090(6), N(4) 0.082(6), N(8) -0.087(6) Å from the least squares plane through these basal donor atoms]. The N(1)-Co-N(4) angle of the six-membered chelate ring of **1** is larger than the N-Co-N angles of the five-membered chelate rings. Also, the axial Co-N(3) and Co-N(5) linkages are not perfectly perpendicular to the CuN₄ plane with N(3)-Co-N and N(5)-Co-N angles ranging from 90.7(5) to 99.3(1)°. The coordinated azido groups which act as a monodentate ligand are slightly asymmetric [N(5)-N(6)=1.223(17) Å and N(6)-N(7)=1.171(17) Å; N(8)-N(9)=1.192(17) Å and N(9)-N(10)=1.140(16) Å] and linear within the experimental error [N(5)-N(6)-N(7)=172.2(15)° and N(8)-N(9)-N(10)=175.6(18)°]. The Co-N(5)-N(6) and Co-N(8)-N(9) angles related to the azide ligand are 126.2(10)° and 123.3(11)°, respectively. The geom-

etry of the diazido-tetraaza macrocyclic cobalt(III) complex **1** depends on the nature of the macrocyclic tetraaza ligand. Due to the asymmetric and flexibility of the tetraaza ring of the 13-membered macrocycle (13-aneN₄), the four nitrogen donors of the macrocycle can not adopt a planar geometry and hence enforces the formation of the octahedral complex, leaving two vacant *cis* positions available for binding two monodentate azido ligands.¹⁶ In contrast, the symmetric and remarkable rigidity of the 14-membered tetraaza macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,18},0^{7,12}]docosane (dttdd) compared to (13-aneN₄) may lead to the formation of octahedral complex of *trans* geometry.⁸ In this case, four nitrogen donors are oriented coplanar with the central metal ion leaving the two axial positions for binding the azido ligands leading to simple nuclear species *trans*-[Co(dttdd)(N₃)₂]N₃·2H₂O.⁸ Interestingly, the secondary amines of the macrocycle are hydrogen bonded

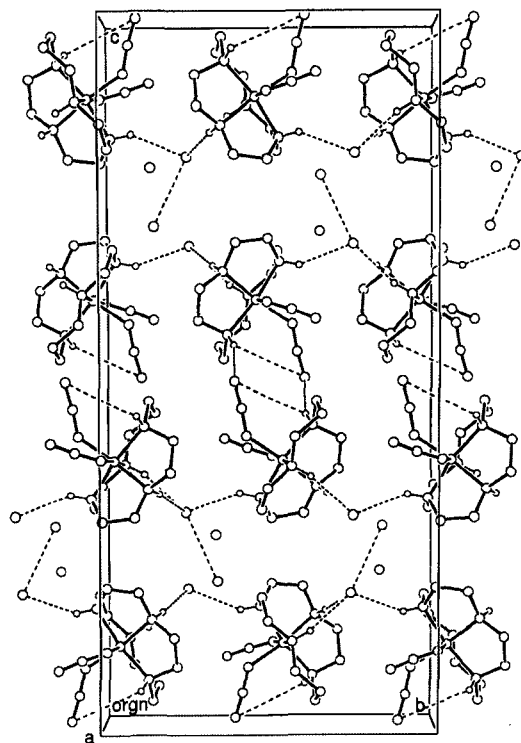
**Fig. 2. View of 1D hydrogen-bonded polymeric chain structure of 1, showing the hydrogen bonds as dotted lines.**

Table 4. Hydrogen Bonding Parameters (Å, °) for 1

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)-H(1)...Cl(1)#4	0.91	2.46	3.345(12)	165.3
N(2)-H(2)...Cl(1)#3	0.91	2.57	3.377(11)	148.7
N(3)-H(3)...Cl(1)#4	0.91	2.47	3.382(11)	174.5
N(4)-H(4)...N(7)#1	0.91	2.08	2.939(19)	157.0
Ow(1)...Cl(1)#5			3.317(13)	
Ow(1)...Cl(1)#6			3.361(14)	

Symmetry codes: (#1) $-x, -y+1, -z$; (#2) $x+1/2, -y+3/2, -z$; (#3) x, y, z ; (#4) $-x+1/2, y+1/2, z$; (#5) $x+1, y, z$; (#6) $x-1/2, y, -z-1/2$.

to chloride anion and nitrogen atom of the azido ligand [N(1)...Cl(1)#4 3.345(12) Å, 165.3°; N(2)...Cl(1)#3 3.377(11) Å, 148.7°; N(3)...Cl(1)#4 3.382(11) Å, 174.5°; N(4)...N(7)#1 2.939(19) Å, 157°; symmetry codes: (#1) $-x, -y+1, -z$; (#2) $x+1/2, -y+3/2, -z$; (#3) x, y, z ; (#4) $-x+1/2, y+1/2, z$]. Furthermore, the water molecule found in the lattice also forms hydrogen bonds with chloride anion [Ow(1)...Cl(1)#5 3.317(13) Å; Ow(1)...Cl(1)#6 3.361(14) Å; symmetry codes: (#5) $x+1, y, z$; (#6) $x-1/2, y, -z-1/2$]. This interaction, as shown in Fig. 2 and Table 4, gives rise to the one dimensional hydrogen-bonded polymer.

The IR spectrum of complex **1** shows bands at 3174 and 3184 cm^{-1} , which are assigned to the $\nu(\text{N-H})$ of the coordinated secondary amines of the macrocycle. Two strong bands at 2020 and 2062 cm^{-1} was assigned to $\nu_{\text{as}}(\text{N}_3)$ stretching of the coordinated azido ligand,¹⁷⁾ which are in agreement with the crystal structure of **1**.

4. Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters are available from author K.-Y. Choi on request.

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