

Notes

Synthesis and Crystal Structure of $[\text{Co}(\text{L})(\text{CO}_3)]\text{ClO}_4$ with Aminoalkyl Pendant-arm [12]aneN3

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The coordination chemistry of a variety of long chain and macrocyclic ligands with nitrogen donor atoms has been well studied with considerable attention focussing on kinetically inert metal ions such as Co(III) and Cr(III).¹⁻³ Particularly, studies on the transition metal complexes of four coordinating ligand are stimulated by interest in developing various model compounds. It was reported that the cobalt(III) complexes with tetraamine ligands such as 3,3,3-tetren or trpn can be very efficient in promoting the hydrolysis of phosphate diesters.² Chin and co-worker³ have reported that $[\text{Co}(\text{cyclen})(\text{H}_2\text{O})_2]^{3+}$ was an excellent catalyst for hydrating nitriles to amides. Although these cobalt(III) complexes with none-cyclic tetraamine ligands are quite common,³ the Co(III) complexes with tetrahedrally coordinating macrocyclic ligands are not well reported.⁴

Investigation of the coordination chemistry of pendant arm macrocycles has drawn considerable attention in recent years. The first transition metal (Ni^{2+} , Cu^{2+} etc.) complexes of tetraaza macrocycles and all group substitute pendant arm tetra- or triaza macrocycles were many reported.^{1,5} Few papers on a single pendant arm triazamacrocycles have also been reported.^{6c} However, Co(III) complexes with [12]aneN3 with aminoalkyl pendant arm have not been synthesized yet.

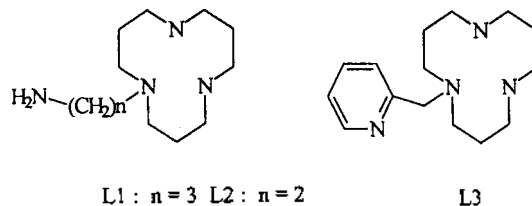
In this papers, we describe the syntheses of the $[\text{Co}(\text{L})(\text{CO}_3)]^+$ and the structure of the octahedral $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$ has been used to determine by X-ray crystallography.

Experimental

Measurement. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. Electronic absorption spectra were obtained on a Gilford Response spectrophotometer. ¹H NMR spectra were obtained on a Bruker ARX 300 MHz FT-NMR spectrophotometer in D₂O with DSS (sodium 2,2-dimethyl-2-silapentane sulfonate) as an internal reference. Elemental Analyses were a performed by Central Laboratory in Gyeongsang National University.

Synthesis. All chemicals were of reagent grade and were used without futher purification.

The lariat triazamacrocycles, 1-(2-aminopropyl)-1,5,9-triazacyclododecane(L1) and 1-(2-aminoethyl)-1,5,9-triazacyclododecane(L2) were prepared by the modified Moore methods.^{6a} 1-(2-pyridylmethyl)-1,5,9-triazacyclododecane(L3) was prepared by reaction of equimolar [12]aneN3 and picolyl chloride in dry DMF solution.¹



The cobalt(III) complexes were prepared from molar equivalents of ligands and $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$. The $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ salt was added to an aqueous solution of 1-2-(aminopropyl)-1,5,9-triazacyclododecane-nHBr(L1), and the mixture was heated in a water bath until evolution of CO_2 was ceased. The resulting red solution was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was mixed with ethanol-water to extract the complex. The extract was evaporated again to dryness giving a red solid. It was dissolved in water, and the solution was applied on the small column of SP-sephadex C-25 cation exchange resin. The absorbed band was slowly eluted with an aqueous 0.1 mol/dm³ NaClO_4 solution. The elutant was mixed with a minimum amount of HClO_4 and LiClO_4 in ethanol. The single crystal used for X-ray measurement was obtained by slow evaporation through the vessel of water-ethanol.

$[\text{Co}(\text{L2})(\text{CO}_3)]\text{ClO}_4$ and $[\text{Co}(\text{L3})(\text{CO}_3)]\text{ClO}_4$ complexes were prepared by an analogous method. All products were recrystallized from water-ethanol. The complex was initially characterized from spectroscopic data.

Results and discussion

The UV/Vis spectrum of $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$ in water shows bands at 544 nm [${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}(\nu_1)$] and 371 nm [${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}(\nu_2)$] typical of Co(III) complexes with $\text{Co}(\text{III})\text{N}_4\text{O}_2$ chromophore. All of these carbonato complexes show electronic spectra similar to those of $[\text{Co}(\text{cyclen})(\text{CO}_3)]^+$ and $[\text{Co}(\text{trpn})(\text{H}_2\text{O})_2]^{3+}$.

The molecular structure of typically $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$ is shown Figure 1 which includes some selected bond parameters.

Figure 1 is showing the heavy atom numbering scheme. Selected bond lengths(A) and angles($^\circ$): Co-O1 1.922(6), Co-O2 1.915(5), Co-N1 2.016(7), Co-N2 2.000(8), Co-N3 1.989(8), Co-N4 1.972(8), N1-C3 1.54(1), , N1-C4 1.52(1),

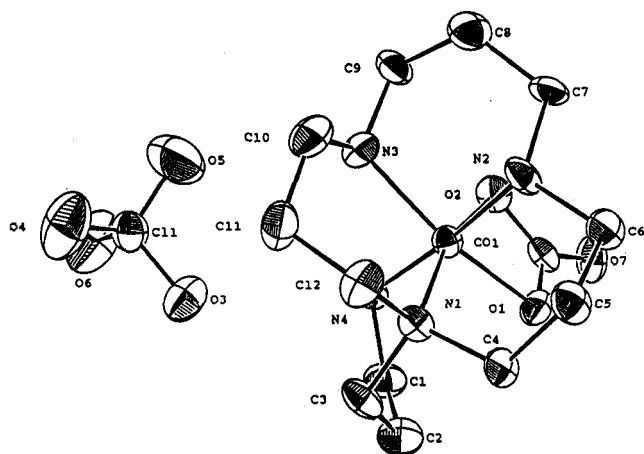


Figure 1. Molecular structure of $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$.

N1-C12 1.51(1), N2-C6 1.53(1), N2-C7 1.51(1), N3-C9 1.50(1), N4-C1 1.53(2), C1-C2 1.57(2), C2-C3 1.54(1), C4-C5 1.55(1), C5-C6 1.56(1), C7-C8 1.53(2), C8-C9 1.52(1), C10-C11 1.53(2), C11-C12 1.57(2) O1-Co-O2 68.9(3), O1-Co-N1 95.4(3), O1-Co-N2 94.4(3), O1-Co-N3 163.1(3), O1-Co-N4 90.4(3), O2-Co-N1 164.3(3), O2-Co-N2 93.3(3), O2-Co-N3 94.2(3), O2-Co-N4 86.5(3), N1-Co-N2 88.9(3), N1-Co-N3 101.4(3), N1-Co-N4 174.8(4), N2-Co-N3 86.6(4), N2-Co-N4 174.8(4), N3-Co-N4 88.2(3).¹⁾

The $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$ crystal consists of $[\text{Co}(\text{L1})(\text{CO}_3)]^+$ cation and ClO_4^- anion. A perspective view of the complexes and atomic labeling scheme is shown Figure 1 and 2. The molecular structure of the $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$ shows a slightly distorted octahedral geometry about the Co(III) center. Four sites are occupied by the nitrogens of L1. The 12-membered ring provides a facial plane of three nitrogen donors, whilst the pendant arm provides the apex. Although

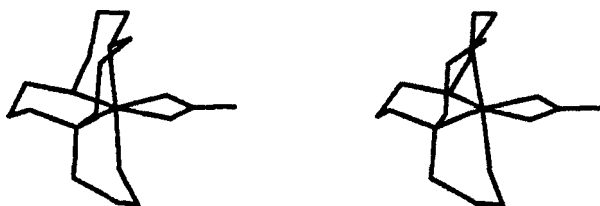


Figure 2. Stereoview of $[\text{Co}(\text{L1})(\text{CO}_3)]^+$ molecular structure.

¹⁾ Crystal data: $\text{Co}_1\text{N}_4\text{O}_7\text{C}_{13}\text{Cl}_4$, $M=418.55$, red-purple, monoclinic, space group $P2_1/c$, $a=13.745(5)$, $b=9.051(1)$, $c=15.765(5)$ Å, $\beta=115.67(3)$, $Z=4$, $F(000)=824$, $U=1768(1)$ Å³, $D_c=2.056$ g cm⁻³, Mo-K α radiation, $\mu(\text{Mo-K}\alpha)=12.1$ cm⁻¹, refinement converged $R1=0.067$, $wR2=0.079$.

$[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$: Yield 72%, Anal. Calcd for C, 34.94; H, 6.28; N, 12.54. Found: C, 34.41; H, 5.89; N, 12.43

$[\text{Co}(\text{L2})(\text{CO}_3)]\text{ClO}_4$: Yield 76%, Anal. Calcd for C, 33.30; H, 6.01; N, 12.95. Found: C, 33.37; H, 5.77; N, 12.42

$[\text{Co}(\text{L3})(\text{CO}_3)]\text{ClO}_4$: Yield 76%, Anal. Calcd for C, 38.43; H, 5.55; N, 11.95. Found: C, 38.21; H, 5.43; N, 12.25

the average bond length Co-N_{av} is 2.00 Å, $\text{Co-N}_{\text{primary}}$ is shorter than $\text{Co-N}_{\text{tertiary}}$. The fragment C-N-C is rather disordered, the chelate rings in the macrocyclic part of the ligand clearly adopt chair conformation. The pendant arm chelates in the twist-boat conformation. The Co-N distances in $[\text{Co}(\text{L1})(\text{CO}_3)]\text{ClO}_4$ are somewhat larger than one might expect for small Co(III) low spin center coordinated to a secondary amine due to intermolecular repulsion of chelate rings.

The obtained Co(III) carbonato complexes, $[\text{Co}(\text{L})(\text{CO}_3)]^+$ are very useful starting point for the preparation of other $[\text{Co}(\text{L})\text{X}_2]^{p+}$ complexes. Therefore, high yield synthetic methods are of great practical interest.

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