

Coordination Modes and Properties of Ag(I) Complex with N,N,N',N',N''-Pentamethyldiethylenetriamine

In Sung Chun, Jung Ah Kwon, Myung Nam Bae, Shim Sung Lee,[†] and Ok-Sang Jung*

Department of Chemistry (BK21) and Center for Plastic Information System, Pusan National University, Busan 609-735, Korea. *E-mail: oksjung@pusan.ac.kr

[†]Department of Chemistry, Gyeongsang National University, Jinju 660-701, Korea

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The reaction of AgClO₄ with acyclic potential tridentate N,N,N',N',N''-pentamethyldiethylenetriamine (pmdeta) has given colorless crystals suitable for X-ray crystallography. The crystal structure (*P*2₁/*n*, *a* = 14.413(1) Å, *b* = 25.270(2) Å, *c* = 16.130(1) Å, *b* = 103.012(1)°, *V* = 5723.7(8) Å³, *Z* = 4, *R* = 0.0349) has been solved and refined. Three silver(I) ions connect four pmdeta ligands to produce discrete complex of [Ag₃(pmdeta)₄](ClO₄)₃. A pmdeta ligand is bridged to three silver(I) ions, and three other pmdeta ligands are chelated to each silver(I) center in a tridentate mode. Thus, the product is a rare tri-nuclear silver(I) complex with two different chemical environments. ¹³C NMR and MAS ¹³C NMR indicate that the tri-nuclear silver(I) complex is not rigid in solution. The contact angles and thermal analyses of the complex are measured and discussed.

Key Words : Coordination mode, MAS ¹³C NMR, N,N,N',N',N''-Pentamethyldiethylenetriamine, Silver(I) complex

Introduction

A variety of coordination modes of Ag(I) ion produce a stream of unusual structures with various types of donor ligands.^{1,2} An important feature of silver(I) ion is the great tendency to form various aesthetic supramolecular architectures.¹ Many silver(I) salts are readily available, and their (counter)anions play an important role in the formation of functional supramolecular materials.³⁻⁸ In particular, silver(I) complexes with acyclic tridentate nitrogen ligands are increasing interest owing to both structural and bioactive features.⁹⁻¹² Furthermore, silver(I) coordination chemistry remains as a challenging theme because the bonds around silver(I) ion have been known to be labile.^{13,14} Such labile properties have been exploited to the development of useful membrane and silver nanoparticle.¹⁵

In an effort to elucidate both the bonding mode of acyclic potential tridentate N donor and the behavior of the Ag(I)-N bond in solution, AgClO₄ complex with N,N,N',N',N''-pentamethyldiethylenetriamine (pmdeta) was prepared and characterized. Herein we describe the structure, coordination mode, and related properties of the discrete product. To our knowledge, this work represents the coordination mode and solution-behavior of a rare tri-nuclear silver(I) complex with simple acyclic tridentate donor.

Experimental Section

Materials and Physical Measurements. AgClO₄ and pmdeta were purchased from Aldrich and used as received. Elemental microanalyses (C, H, N) were performed on crystalline samples by the Advanced Analytical Center at KIST using a Perkin Elmer 2400 CHNS analyzer. Contact

angle was evaluated with a Krüss GmbH Drop Shape Analysis for DSA 100. Thermal analyses were carried out under a nitrogen atmosphere with a rate of 5 °C/min using a Stanton Red Croft TG 100. Infrared spectrum was obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with sample prepared as KBr pellet. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Plus 300 MHz FT NMR spectrometer. The chemical shifts were relative to internal Me₄Si. MAS ¹³C NMR spectrum was taken on a Bruker DSX 400 MHz FT NMR spectrometer.

Preparation of [Ag₃(pmdeta)₄](ClO₄)₃. An aqueous solution (5 mL) of pmdeta (0.35 mmol, 60 mg) was slowly dropped into an aqueous solution (20 mL) of AgClO₄ (0.30 mmol, 63 mg), and stirred for 1 h at room temperature. The reaction solution was reduced to 10 mL, filtered, and left at 5 °C to obtain the colorless crystals in 70% yield based on Ag(I) ion. mp 140 °C (dec). Anal. Calcd for C₃₆H₉₂N₁₂O₁₂Cl₃Ag₃: C, 32.88; H, 7.05; N, 12.78. Found: C, 32.40; H, 7.07; N, 12.14. IR (KBr, cm⁻¹): 2957 (m), 2819 (s); 1458 (s), 1299 (m), 1092 (s, *ν*(ClO₄)), 938 (m), 781 (m), 629 (s).

The explosive compound containing perchlorate should be carefully treated!

Crystallographic Structure Determinations. X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K α radiation (λ = 0.71073 Å) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ -scan method. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix

Table 1. Crystallographic Data for $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$

Empirical formula	$\text{C}_{36}\text{H}_{92}\text{N}_{12}\text{O}_{12}\text{Cl}_3\text{Ag}_3$
Formula weight	1315.18
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 14.413(1)$ Å $b = 25.270(2)$ Å $c = 16.130(1)$ Å $\beta = 103.012(1)^\circ$
Volume	$5723.7(8)$ Å ³
Z	4
Density (calculated)	1.526 Mg/m^3
Absorption coefficient	1.217 mm^{-1}
F(000)	2720
Crystal size	$0.35 \times 0.25 \times 0.10 \text{ mm}^3$
θ range for data collection	1.53 to 26.37°
Index ranges	$-18 \leq h \leq 18$, $-28 \leq k \leq 31$, $-12 \leq l \leq 20$
Reflections collected	33374
Independent reflections	11666 [R(int) = 0.0334]
Completeness to $\theta = 26.37^\circ$	99.7%
Absorption correction	Empirical (SADABS)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11666 / 0 / 595
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0349, wR2 = 0.0729
R indices (all data)	R1 = 0.0617, wR2 = 0.0835
Largest diff. peak and hole	0.686 and -0.514 e/Å^{-3}

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^2}^{1/2}$$

least squares techniques (SHELXL 97).¹⁶ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-601330). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/per/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis. Reaction of AgClO_4 with pmdeta gave colorless crystals of $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$ suitable for X-ray crystallography (eq. 1). The product was obtained in high yield irrespective of the mole ratios, indicating that the product is very stable species. However, when pmdeta ligand was treated at a ten-fold excess, no solid product was precipitated even after 4 weeks. The crystalline product is insoluble in common organic solvents, but is very slightly

soluble in water. The compound seems to be dissociated in very polar solvents such as N,N'-dimethylformamide, acetonitrile, and dimethylsulfoxide.

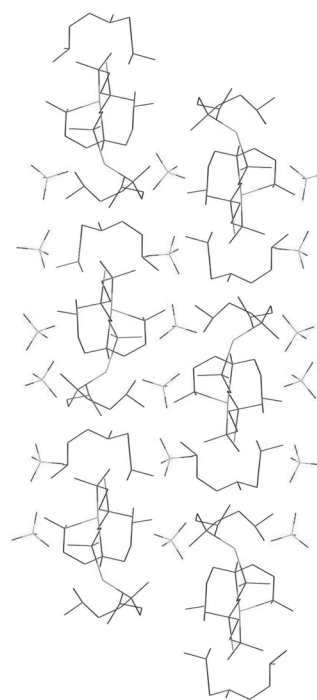
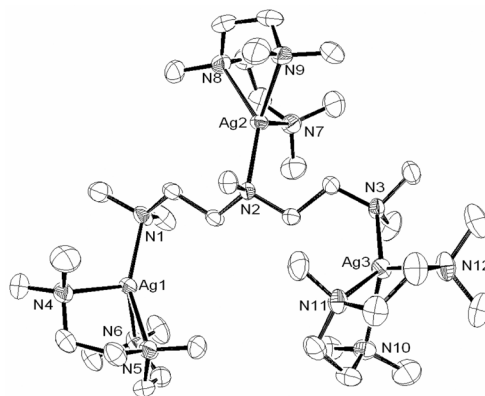
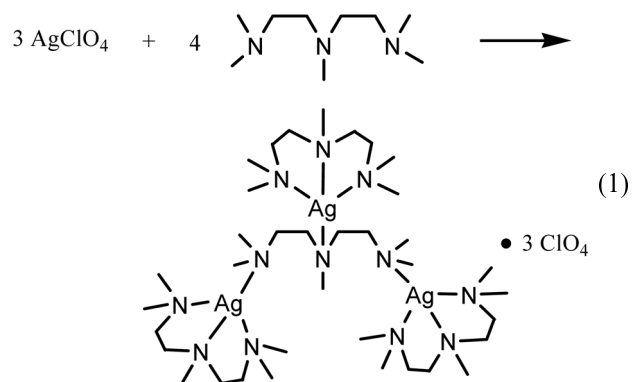


Figure 1. ORTEP drawing (up, 50% probability) and molecular packing diagram (down) of $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$. For ORTEP drawing, the anions and hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$

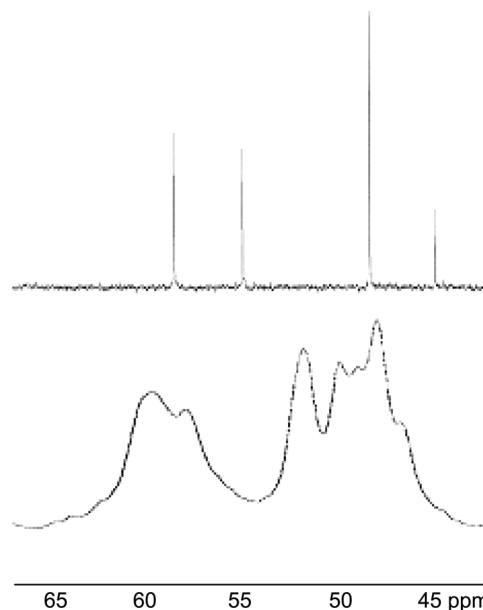
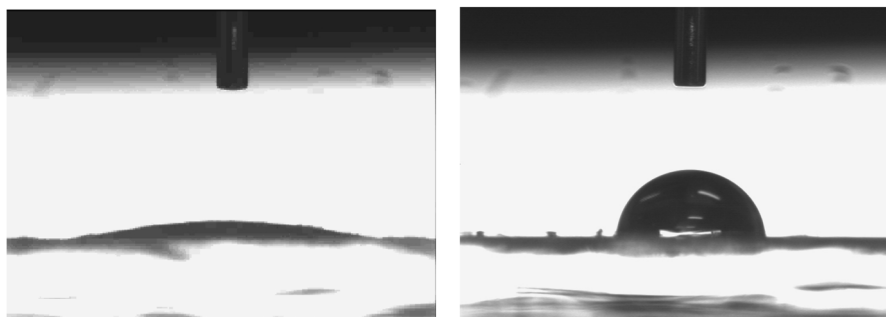
Ag(1)-N(1)	2.271(3)	Ag(2)-N(9)	2.420(3)
Ag(1)-N(6)	2.393(3)	Ag(2)-N(7)	2.440(3)
Ag(1)-N(5)	2.395(3)	Ag(3)-N(3)	2.264(3)
Ag(1)-N(4)	2.447(3)	Ag(3)-N(11)	2.368(3)
Ag(2)-N(2)	2.326(3)	Ag(3)-N(10)	2.439(3)
Ag(2)-N(8)	2.420(3)	Ag(3)-N(12)	2.443(3)
N(1)-Ag(1)-N(6)	117.7(1)	N(2)-Ag(2)-N(7)	119.4(1)
N(1)-Ag(1)-N(5)	147.8(1)	N(8)-Ag(2)-N(7)	76.9(1)
N(6)-Ag(1)-N(5)	78.7(1)	N(9)-Ag(2)-N(7)	113.3(1)
N(1)-Ag(1)-N(4)	114.4(1)	N(3)-Ag(3)-N(11)	139.8(1)
N(6)-Ag(1)-N(4)	116.6(1)	N(3)-Ag(3)-N(10)	121.1(1)
N(5)-Ag(1)-N(4)	76.0(1)	N(11)-Ag(3)-N(10)	77.0(1)
N(2)-Ag(2)-N(8)	142.5(1)	N(3)-Ag(3)-N(12)	119.4(1)
N(2)-Ag(2)-N(9)	117.75(11)	N(11)-Ag(3)-N(12)	77.8(1)
N(8)-Ag(2)-N(9)	78.4(1)	N(10)-Ag(3)-N(12)	111.0(1)

Crystal Structure. The molecular structure of $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$ is shown in Figure 1, and relevant bond lengths and bond angles are listed in Table 2. Three silver(I) ions connect four pmdeta ligands to produce a trinuclear complex of $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$. Two kinds of pmdeta bonding modes, the linear skeletal ligand and the chelated ligands, exist in the crystal structure. A pmdeta ligand connects three silver(I) ions, and three other pmdeta ligands are chelated to each silver(I) center in a tridentate mode. Thus, the product is a tri-nuclear silver(I) complex with two kinds of Ag(I) ions in contrast to the known metal complexes with 3 N donor ligands.¹⁰⁻¹² The Ag(I)-N distances are in the range of 2.271(3)-2.447(3) Å. The Ag(I)-N bond lengths formed from the linear skeletal pmdeta ligand are shorter than the corresponding bonds from the chelated pmdeta ligands, presumably owing to the presence of angle strain in the chelated pmdeta ligands. Thus, even though the local geometry around all silver(I) ions ($\text{Ag}(\text{I})\text{N}_4$) is a tetrahedral arrangement, the N-Ag(I)-N angles around the chelated pmdeta ligands are severely bent (76.0(1)-78.7(1)°) from the tetrahedral arrangement. Concomitantly, the corresponding angles around the linear pmdeta are splayed out. All bond angles around silver(I) ions are in the range of 76.0(1)-147.8(1)°. Perchlorate ClO_4^- is positioned

as a simple counteranion (the shortest distance $\text{Ag}\cdots\text{O}(\text{ClO}_4^-) = 4.24$ Å). In the packing structure, cationic complexes and counteranions are alternatively layered.

The coexistence of two kinds of bonding modes of 3 N donor is rare in contrast to simple tridentate or bridged tridentate.¹⁰⁻¹² Another observation is that the Ag(I)-N of the skeletal pmdeta is shorter than that of the chelated pmdeta. There are no significant interactions between adjacent molecules.

Solution-Behavior and Physicochemical Properties. In order to elucidate the delicate difference of two bonding modes, ^1H and ^{13}C NMR spectra in $\text{Me}_2\text{SO}-d_6$ and acetonitrile- d_3 were investigated. The NMR spectra suggest that the ligand unit is dissociated in solution: the ^1H and ^{13}C NMR spectra of the complex are consistent with that of the ligand itself in solution. Such a fact indicates that the Ag-N bonds are labile in solution.¹⁰ Four ^{13}C peaks in the range of 44-58 ppm clearly signify that all pmdeta ligands are dissociated. The solid state MAS ^{13}C NMR spectrum was obtained in order to compare the ^{13}C NMR in the solution (Figure 2). Two sets of ^{13}C chemical shifts in the solid state

**Figure 2.** ^{13}C NMR in $\text{Me}_2\text{SO}-d_6$ (top) and MAS ^{13}C NMR (bottom) spectra of $[\text{Ag}_3(\text{pmdeta})_4](\text{ClO}_4)_3$.**Figure 3.** Water contact angles of microcrystalline layer on vinyl tape (left) and simple vinyl tape (right).

in the 3 : 1 mole ratio at 47-60 ppm are due to the presence of two kinds of ligands in the solid state. That is, the solid state NMR spectrum is consistent with the X-ray crystal structure.

The present complex is thermally stable up to 140 °C, and decomposes at 140-260 °C and 260-300 °C. In order to understand the hydrophilic properties of the present microcrystals, water contact angles were measured.¹⁷ The microcrystals were layered on the vinyl tape, and the contact angle of microcrystalline layer was compared with that of the polyethylene tape. As shown in Figure 3, the crystalline layer showed higher contact angle than that of vinyl tape, indicating that the microcrystals are hydrophilic. The water-wettability of the compound may be induced by the strong hydrogen-bonds not only between ClO₄⁻ anions on the crystalline surface and water molecules, but also between ligands and water molecules. Considering various factors including anions and solvate molecules, further experiments aimed at structure-properties relationships are in progress.

In conclusion, we have prepared a rare discrete silver(I) complex with “two kinds of coordination modes of 3 N donors”. The behaviors of bonding modes in solution and solid state were elucidated by ¹³C NMR spectra. Understanding the key factors of labile properties and hydrophilicity may be devoted to the development of membrane materials that can discriminate various alkene groups.

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