**Table IV.** Hydrogen Bonds (X–H⋯Y) for Be(C₆H₄OCO₂)(OH₂)₂[a]

| X–H⋯Y | X–H, Å | H⋯Y, Å | X⋯Y, Å | X–H⋯Y, deg |
|---|---|---|---|---|
| O4–H5⋯O1(a) | 0.965 | 1.628 | 2.592 | 178.4 |
| O4–H6⋯O3(b) | 0.874 | 1.843 | 2.704 | 167.7 |
| O5–H7⋯O2(c) | 0.908 | 1.809 | 2.695 | 164.5 |
| O5–H8⋯O2(d) | 0.936 | 1.744 | 2.672 | 171.1 |

[a]Symmetry positions of atom Y: (a) $x$, $1.5 - y$, $0.5 + z$; (b) $2 - x$, $1 - y$, $1 - z$; (c) $2 - x$, $1 - y$, $-z$; (d) $2 - x$, $0.5 + y$, $0.5 - z$.

standing of the toxicity of beryllium[1]—the ⁹Be NMR shows one singlet at ca. 0.8 ppm.[21] The observation of only one ⁹Be singlet does not exclude the presence of other beryllium-containing species in solution, however, because fast ligand exchange on the NMR time scale could cause averaged spectra.

## Discussion

The present investigation proves the identity of the sample Be(C₆H₄OCO₂)(OH₂)₂ as a chelate complex, but of course, does not exclude the existence of Be(C₆H₄OCO₂)·3H₂O and Be(OH)(C₆H₄OHCO₂)·2H₂O, which may well be components of the complex equilibria present in aqueous solutions of beryllium(II).[10] Small modifications of the preparation of beryllium salicylate could lead to different products. The straightforward formation of Be(C₆H₄OCO₂)(OH₂)₂ at pH 4.8 is noteworthy as compared to the behavior of other divalent metal ions toward the salicylate ligand. Although many salicylate salts of the stoichiometry M(C₆H₄OHCO₂)₂ (M = divalent metal ion) are known,[22–25] only a few salts of the stoichiometry M(C₆H₄OCO₂) have been isolated.[26] To the best of our knowledge, no beryllium compound of the stoichiometry Be(C₆H₄OHCO₂)₂ has been reported. In light of the ubiquitous availability of phenolic and carboxylic groups in many natural products, the finding of strong bonding of Be²⁺ to these functions is very important. This is particularly true since the chelation appears to persist in aqueous solution under physiological conditions of temperature, concentration, and pH and may thus be relevant for metal transport and for fixation at specific coordination sites in biopolymers.

**Supplementary Material Available:** Tables giving details of the structure analysis, atomic positions, anisotropic thermal parameters, and hydrogen atom parameters (5 pages); a table of observed and calculated structure amplitudes (8 pages). Ordering information is given on any current masthead page.

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## Encapsulation of Silver(I) by the Crown Thioether Ligand 1,3,6,9,11,14-Hexathiacyclohexadecane (16S6). Synthesis and Structure of [Ag(16S6)][ClO₄]

Broer de Groot and Stephen J. Loeb*

Although the most common coordination numbers for Ag(I) are 2 and 4,[1] the complexing of Ag(I) by crown thioether ligands

**Table I.** Crystallographic Data for [Ag(16S6)][ClO₄]

| chem formula | C₁₀H₂₀AgClO₄S₆ | $\rho$(calcd), g/cm⁻³ | 1.86 |
|---|---|---|---|
| fw | 540.04 | $Z$ | 8 |
| $a$, Å | 9.842 (2) | $\mu$, cm⁻¹ | 18.10 |
| $b$, Å | 25.748 (4) | $\lambda$, Å | 0.710 69 |
| $c$, Å | 15.217 (2) | $T$, °C | 23 |
| space group | *Pbca* (No. 61) | $R(F_o)$, % | 5.59 |
| $V$, Å³ | 3856 (2) | $R_w(F_o)$, % | 6.48 |

has produced a variety of homoleptic thioether complexes of higher coordination numbers. For example, six-coordination has been achieved for [Ag(18S6)]⁺ (18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane)[2] and [Ag(9S3)₂]⁺ (9S3 = 1,4,7-trithiacyclononane),[3–5] five-coordination was observed in the dimeric complex [Ag₂L₂]²⁺ (L = 2,5,7,10-tetrathia[12](2,5)thiophene),[6] and four-coordination was found for [Ag₃(9S3)₃]³⁺, [Ag₂(15S5)₂]²⁺ (15S5 = 1,4,7,10,13-pentathiacyclopentadecane), and [Ag(TT-[9]OB)₂]⁺ (TT[9]OB = 2,5,8-trithia[9]-*o*-benzenophane).[5,7,8] Of these thioether macrocycles, only 18S6 acts as a classical macrocyclic ligand, providing all the donor atoms from a single ligand and encapsulating the Ag⁺ ion to form a simple mononuclear species. We have recently demonstrated that the thioether macrocycle 1,3,6,9,11,14-hexathiacyclohexadecane (16S6) can act as a tetradentate ligand in which four of the six S atoms define a tetrahedral coordination sphere.[9]
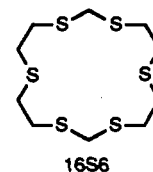


16S6

We describe herein the synthesis and X-ray structure determination of [Ag(16S6)][ClO₄], in which the thioether macrocycle 16S6 acts as a tetradentate ligand for Ag(I). This results in encapsulation of the Ag(I) ion in a homoleptic thioether coordination sphere with distorted tetrahedral geometry.

## Experimental Section

1,3,6,9,11,14-Hexathiacyclohexadecane (16S6) was prepared by the published method.[9] AgClO₄, CH₃CN, and all deuterated solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of N₂ by using standard Schlenk techniques, and all solvents were degassed prior to use. ¹H and ¹³C{¹H} NMR spectra were recorded at 300.1 and 75.4 MHz, respectively, on a Brüker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Microanalytical Services, New Westminister, British Columbia, Canada. Cyclic voltammetric experiments were performed by using a BAS CV-27 potentiostat with a platinum-disk working electrode, a Ag/AgCl reference electrode, and [NBu₄][PF₆] as the supporting electrolyte. All potentials are quoted versus ferrocene/ferrocenium, Fc/Fc⁺.

**Preparation of [Ag(16S6)][ClO₄].** *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.* To a stirred

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**Table II.** Selected Positional Parameters and $B(eq)$ Values for [Ag(16S6)][ClO$_4$]

| atom | $x$ | $y$ | $z$ | $B(eq)$, Å$^2$ |
|------|-----|-----|-----|-------|
| Ag | 0.2843 (1) | 0.1238 (1) | 0.6088 (1) | 5.53 (5) |
| S1 | 0.1474 (2) | 0.2082 (1) | 0.6083 (2) | 5.1 (1) |
| S2 | 0.3314 (3) | 0.2130 (1) | 0.7699 (2) | 5.7 (1) |
| S3 | 0.4012 (3) | 0.0836 (1) | 0.7433 (2) | 5.6 (1) |
| S4 | 0.1595 (2) | 0.0381 (1) | 0.5925 (1) | 4.5 (1) |
| S5 | 0.3710 (3) | 0.0394 (1) | 0.4437 (2) | 6.3 (1) |
| S6 | 0.4507 (3) | 0.1657 (1) | 0.5027 (2) | 5.4 (1) |
| C1 | 0.1998 (9) | 0.2428 (4) | 0.7059 (8) | 5.7 (6) |
| C2 | 0.239 (1) | 0.1594 (5) | 0.8206 (7) | 6.8 (7) |
| C3 | 0.328 (1) | 0.1146 (5) | 0.8399 (7) | 7.1 (7) |
| C4 | 0.312 (2) | 0.222 (4) | 0.7439 (9) | 9.0 (8) |
| C5 | 0.277 (1) | 0.0029 (5) | 0.6610 (9) | 8.3 (8) |
| C6 | 0.2137 (11) | 0.0139 (4) | 0.4874 (8) | 6.3 (6) |
| C7 | 0.3162 (11) | 0.0976 (5) | 0.3913 (6) | 5.6 (6) |
| C8 | 0.421 (1) | 0.1395 (5) | 0.3934 (6) | 6.8 (7) |
| C9 | 0.375 (2) | 0.2267 (6) | 0.5049 (11) | 12 (1) |
| C10 | 0.248 (1) | 0.2375 (5) | 0.5209 (11) | 10 (1) |

solution of AgClO$_4$ (125 mg, 0.601 mmol) in CH$_3$CN (10 mL) was added 16S6 (200 mg, 0.601 mmol) dissolved in CH$_2$Cl$_2$ (5 mL). The resulting clear, colorless solution was stirred for a further 4 h and the solvent removed in vacuo. The crude white solid product was recrystallized from CH$_3$CN/diethyl ether. Yield: 286 mg (88%). $^{13}$C{$^1$H} NMR (CD$_3$CN): $\delta$ 38.88 (SCH$_2$S), 35.75, 33.92 (SCH$_2$CH$_2$S). $^1$H NMR (CD$_3$CN): $\delta$ 3.80 (s, SCH$_2$S) 3.06 (m, SCH$_2$CH$_2$S). IR: $\nu$(ClO) 1089 cm$^{-1}$ (vs, br). Anal. Calcd for C$_{10}$H$_{20}$AgClO$_4$S$_6$: C, 22.24; H, 3.74; S, 35.63. Found: C, 22.54; H, 3.61; S, 35.16.

**Chemical Oxidation of [Ag(16S6)][ClO$_4$].** The transient blue [Ag(16S6)]$^{2+}$ ion results from the addition of either H$_2$SO$_4$ (98%) or HClO$_4$ (70%) to a sample of [Ag(16S6)]$^+$. The oxidized product is stable at room temperature for only a few seconds, even in this highly acidic aqueous media.

**Structure Determination of [Ag(16S6)][ClO$_4$].** Colorless crystals of [Ag(16S6)][ClO$_4$] were grown by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement by using the setting angles of 25 centered reflections. Machine parameters, crystal data, and data collection parameters are summarized in Table I and detailed in Table S–I (deposited as supplementary material). The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collection. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with the space group *Pbca*, and this was confirmed by a successful solution refinement. An empirical absorption correction, based on $\psi$-scan data, was applied to the data. A total of 2897 reflections were collected, and 1767 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The data were processed by using the TEXSAN software package[10] running on a VAX 3520 workstation. Refinement was carried out by using full-matrix least-squares techniques on $F$ minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factors. Atomic scattering factors[11] and anomalous dispersion terms[12,13] were included. Fixed H atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

The positions of the silver atom and four of the six sulfur atoms were determined by direct methods from the $E$ map with highest figure of merit. The remaining non-hydrogen atoms were located from a difference Fourier map calculation. In the final cycles of refinement, the silver, chlorine, sulfur, oxygen, and carbon atoms were all assigned anisotropic thermal parameters. This resulted in $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.0559$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0648$ at final convergence. A goodness of fit calculation resulted in a value of 1.77. The $\Delta/\sigma$ value for any parameter in the final cycle was less than 0.002. A final difference Fourier map calculation showed no peaks of chemical signifi-

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**Table III.** Selected Bond Distances and Angles for [Ag(16S6)][ClO$_4$]

| Distances (Å) | | | |
|------|------|------|------|
| Ag–S1 | 2.557 (3) | Ag–S3 | 2.564 (3) |
| Ag–S4 | 2.537 (3) | Ag–S6 | 2.540 (3) |
| S1–C1 | 1.807 (11) | S1–C10 | 1.821 (13) |
| S2–C1 | 1.793 (11) | S2–C2 | 1.822 (12) |
| S3–C3 | 1.820 (12) | S3–C4 | 1.805 (13) |
| S4–C5 | 1.801 (12) | S4–C6 | 1.798 (11) |
| S5–C6 | 1.808 (11) | S5–C7 | 1.780 (11) |
| S6–C8 | 1.818 (11) | S6–C9 | 1.738 (14) |
| C2–C3 | 1.48 (2) | C4–C5 | 1.40 (2) |
| C7–C8 | 1.49 (2) | C9–C10 | 1.31 (2) |
| Ag$\cdots$S2 | 3.390 (3) | Ag$\cdots$S5 | 3.429 (3) |

| Angles (deg) | | | |
|------|------|------|------|
| S1–Ag–S3 | 125.57 (9) | S1–Ag–S4 | 118.88 (9) |
| S1–Ag–S6 | 88.66 (9) | S3–Ag–S4 | 86.83 (9) |
| S3–Ag–S6 | 112.9 (1) | S4–Ag–S6 | 128.26 (9) |
| C1–S1–C10 | 103.9 (7) | C1–S2–C2 | 101.2 (5) |
| C3–S3–C4 | 100.9 (6) | C5–S4–C6 | 98.6 (6) |
| C6–S5–C7 | 102.2 (5) | C8–S6–C9 | 106.5 (7) |
| S1–C1–S2 | 116.2 (5) | S4–C6–S5 | 117.1 (6) |
| S2–C2–C3 | 112.4 (9) | C2–C3–S3 | 114.5 (7) |
| S3–C4–C5 | 115.3 (10) | C4–C5–S4 | 120.1 (11) |
| S5–C7–C8 | 112.8 (8) | C7–C8–S6 | 113.4 (7) |
| S6–C9–C10 | 127.4 (12) | C9–C10–S1 | 124.6 (11) |
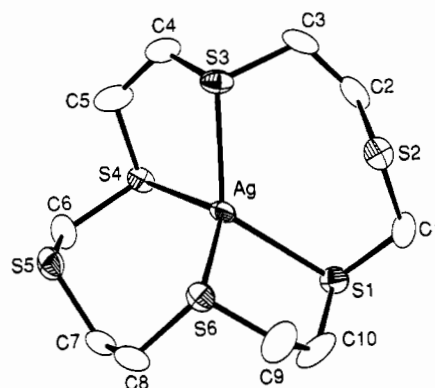


**Figure 1.** Perspective ORTEP drawing of the [Ag(16S6)]$^+$ cation, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

cance; the largest was 0.36 e/Å$^3$ and was associated with the Ag atom. Selected atomic positional parameters are summarized in Table II, and selected bond distances and angles are summarized in Table III. Nonessential atomic positional parameters (Table S-II), nonessential bond distances and angles (Table S-III), thermal parameters (Table S-IV), hydrogen atom parameters (Table S-V), and values of 10|$F_o$| and 10|$F_c$| (Table S-VI) are deposited as supplementary material.

**Results**

The reaction of equimolar amounts of AgClO$_4$ and 16S6 in CH$_3$CN results in a high yield of the mononuclear complex [Ag(16S6)][ClO$_4$]. Figure 1 shows an ORTEP drawing of the cation [Ag(16S6)]$^+$. The Ag(I) ion is bonded in a symmetrical fashion to four of the six thioether donor atoms: Ag–S1 = 2.557 (3), Ag–S3 = 2.564 (3), Ag–S4 = 2.537 (3), and Ag–S6 = 2.540 (3) Å. S2 and S5 are oriented toward the metal center at nonbonding distances: Ag–S2 = 3.390 (3) and Ag–S5 = 3.429 (3) Å. There are three type of S–Ag–S angles, those contained in five- and seven-membered chelate rings and those between the chelate rings. The S1–Ag–S6 and S3–Ag–S4 angles associated with the five-membered rings are 88.66 (9) and 86.83 (9)°, respectively, and the S3–Ag–S6 and S1–Ag–S4 angles associated with the seven-membered rings are 112.9 (1) and 118.8 (9)°. The angles between the chelate rings, S1–Ag–S3 and S4–Ag–S6, are 125.57 (9) and 128.26 (9)°, respectively. This results in a flattened tetrahedral geometry for Ag(I) in which the smaller angles required by the five-membered chelate rings are offset by the larger angles between chelate rings.

The $^1$H NMR spectrum in CD$_3$CN (300 K) shows only a sharp singlet at 3.80 ppm for the SCH$_2$S methylene protons and a sharp

14-line multiplet at 3.05 ppm for the SCH$_2$CH$_2$S protons. The low-temperature spectrum (235 K) shows considerable broadening, but no limiting spectrum could be attained. Since the solid-state conformation of the complex contains five different sets of methylene groups, some type of fluxional process must be occurring. A process in which the nonbonded S atoms, S2 and S5, interconvert with coordinated S atoms, S1 and S6, is most likely. This process would interconvert the five- and seven-membered chelate rings and should be relatively facile, since the conformation of the coordinated 16S6 macrocycle already orients the nonbonded S atoms toward the metal center.
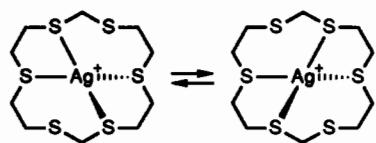


The possibility of oxidation of the Ag(I) cation to a stable Ag(II) species, which has been observed for [Ag(9S3)$_2$]$^+$ and [Ag(18S6)]$^+$, was investigated.[2-4] Cyclic voltammetry of [Ag-(16S6)]$^+$ in CH$_3$CN (0.1 M [NBu$_4$][PF$_6$]) at platinum electrodes showed an oxidation at $E_{pa}$ = 0.87 V versus Fc/Fc$^+$, which is essentially irreversible; only a small return wave was observed, indicating that the oxidized product is unstable in CH$_3$CN at 298 K. Attempts to stabilize the oxidation product in strongly aqueous media by the addition of H$_2$SO$_4$ (98%) or HClO$_4$ (70%) to [Ag(16S6)]$^+$, at 298 K, resulted in the production of a blue solution visible at the surface of the crystals as they dissolved. The color faded very quickly, and the crystals ultimately dissolved to give a clear solution. Although these observations are consistent with the generation of [Ag(16S6)]$^{2+}$, the transient nature of the product prevented a full analysis.

## Discussion

The solid-state structure of [Ag(16S6)]$^+$ shows that the 16S6 macrocycle provides a unique coordination environment for Ag(I). This complex is four-coordinate, with two additional S donor atoms oriented toward the Ag$^+$ ion at distances approximately 0.8 Å longer than the coordinated Ag–S bond lengths. The solution $^1$H NMR data for [Ag(16S6)]$^+$ also indicate that the two additional S atoms can participate in bonding to the metal center via an interconversion of bonded and nonbonded pairs of S donor atoms in the SCH$_2$S fragments. Therefore, the possibility exists that 16S6 could provide a distorted version of the S$_6$ coordination sphere found in [Ag(18S6)]$^+$ and necessary to stabilize Ag(II).[2]
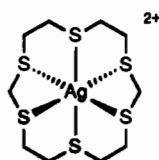


Electrochemically the oxidation chemistry of [Ag(16S6)]$^+$ appears to be similar to that observed for [Ag(18S6)]$^+$ and [Ag(9S3)$_2$]$^+$.[2-4] The homoleptic thioether coordination spheres found in [Ag(18S6)]$^+$, [Ag(9S3)$_2$]$^+$, and [Ag(16S6)]$^+$ result in relatively low oxidation potentials, $E_{pa}$ = 1.00, 0.79, and 0.87 V, respectively. This can be attributed to a higher electron density at the metal center, which promotes oxidation. Stabilization of the deep blue oxidation products [Ag(18S6)]$^{2+}$ and [Ag(9S3)$_2$]$^{2+}$ is a direct result of the pseudooctahedral coordination geometries, which stabilizes Ag(II) with little structural rearrangement.[2] Structural and spectroscopic data suggest six sulfur atoms are involved in coordination to Ag(I) in [Ag(16S6)]$^+$, but the degree to which 16S6 can stabilize the Ag(II) oxidation product is limited. These results demonstrate the unique nature of 16S6 coordination and emphasize the structural requirements of the Ag(I)/Ag(II) redox couple.

Contribution from the Laboratoire de Chimie Moléculaire, UA CNRS 426, Université de Nice, Parc Valrose, 06034 Nice, France, and Laboratoire de Cristallochimie, CNRS UA 254, Campus de Beaulieu, Université de Rennes, 35042 Rennes, France

## Preparation and Structure of a Mixed Niobium(I) Isocyanide Carbonyl Complex with a Bent C–N–C Linkage

Ghazar Aharonian,[1a] Liliane G. Hubert-Pfalzgraf,*,[1a] Abdenasser Zaki,[1a] and Guy Le Borgne[1b]

### Introduction

Inorganic and organometallic complexes in low oxidation states generally require good π-acceptor ligands. While carbon monoxide is a π-acceptor commonly used for this purpose, the isoelectronic isocyanide ligand may also stabilize low-valent species, although it has received less attention. Thus, while niobium carbonyl derivatives range from oxidation states +3 to –3, isocyanide complexes are limited to some trivalent species, ($\eta^5$-Cp)$_2$Nb-(C$_4$H$_9$)(CNR) (R = Ph, Cy),[2] [($\eta^5$-Cp)Nb(CN-*t*-Bu)$_4$Cl]$^+$,[3] Nb$_2$Cl$_6$(CN-*t*-Bu)$_4$($\mu$-*t*-BuNCCN-*t*-Bu),[4] and Nb$_3$Cl$_8$(CN-*t*-Bu)$_5$.[5] No niobium or tantalum isocyanide complexes in oxidation states lower than 2 have been mentioned. We wish now to report the synthesis of the formally niobium(I) NbCl(CO)(*t*-BuNC)(dmpe)$_2$ (dmpe = 1,2-dimethylphosphinoethane) derivative and its structural characterization, which shows the presence of a terminal bent carbene-like isocyanide moiety.

### Experimental Section

All manipulations were routinely performed by using Schlenk tubes and vacuum-line techniques under purified argon. The solvents were purified by standard methods. NbCl$_5$ and dmpe were used as received; tBuNC was dried over molecular sieves. NbCl(CO)$_2$(dmpe)$_2$ was prepared according to the literature.[6] $^1$H NMR and IR spectra were run on Bruker WH-90 and IR-FT S45 spectrometers, respectively. Elemental analysis was performed by the Centre de Microanalyse du CNRS.

**NbCl(CO)(*t*-BuNC)(dmpe)$_2$.** *tert*-Butyl isocyanide (0.39 mL, 3.43 mmol) was added to a suspension of NbCl(CO)$_2$(dmpe)$_2$ (0.92g, 1.71 mmol) in 20 mL toluene at room temperature. The reaction medium was irradiated for 25 h (125 W). Filtration left a beige precipitate (analyzing as Nb$_2$Cl$_2$(CN-*t*-Bu)$_3$(dmpe)) and a red-brown filtrate, which was concentrated and stored at –30 °C. Red crystals of NbCl(CO)(*t*-BuNC)(dmpe)$_2$ (0.4g, 43%), suitable for X-ray, were obtained by precipitation and isolated by filtration. The product is insoluble in toluene and soluble in chloroform or methylene chloride. $^1$H NMR (CD$_2$Cl$_2$, ppm): 1.42, (Me–P, m, 24 H), 0.98 (P–CH$_2$, m, 8 H), 1.24 (*t*-BuNC, s, 9 H). IR (Nujol, cm$^{-1}$): 1871, 1850 ($\nu$(C—O)), 1747 ($\nu$(N≡C)), 300

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