DOI: 10.1002/ejic.200601187

A New Silver(I) Aggregate Having an Octagonal Ag_4S_4 Core Where μ_3-S Bonding Interactions Lead to a Nanotube Assembly that Exhibits Quasiaromaticity

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Keywords: Bioinorganic chemistry / Silver / Aromaticity / Nanotubes

Silver(I) chloride reacts with 2-mercapto-3,4,5,6-tetrahydropyrimidine ($StpmH_2$, $C_4H_8N_2S$) in DMSO with excess triethylamine to give a complex of formula $\{[Ag_4Cl_4(\mu_3\text{-}StpmH_2)_4]_n\}$ (**1**). The product was characterized by elemental analyses, FTIR far-IR, UV/Vis, and ^1H and ^{109}Ag NMR spectroscopic techniques. The ^{109}Ag NMR spectroscopic data of the complexes $\{[Ag_6(\mu_2\text{-}Br)_6(\mu_2\text{-}StpmH_2)_4(\mu_3\text{-}StpmH_2)_2]_n\}$ (**2**) and $\{[Ag_4(\mu_2\text{-}StpmH_2)_6](NO_3)_4\}_n$ (**3**) are also reported here for comparison. Crystal structure of complex **1** was determined by X-ray diffraction at 100(1) K. Complex **1**, $C_4H_8AgClN_2S$, crystallized in the tetragonal system, space group *P4cc*, a = 15.7761(9) Å, b = 15.7761(9) Å, c = 6.9624(8) Å, V = 1732.8(2) Å^3, Z = 2. Each metal ion is bonded to one terminal Cl atom and three μ_3-S atoms from three $StpmH_2$ ligands. Four silver ions are bridged by four sulfur atoms forming an octagonal Ag_4S_4 core. Each Ag^I ion of one core is also bridged to an Ag^I ion of another core through a sulfur atom, which forms an infinite nanotube structure. A computational study utilizing the method of nucleus-independent chemical shifts (NICS) showed that the Ag_4S_4 core exhibits strong quasiaromaticity at the geometric cage center. To the best of our knowledge, this is the first example of an Ag^I cluster that presents quasiaromaticity and stacking interactions.

Introduction

The research in designing infinite molecular components with specific chains and networks is a matter of current interest.[1] This self-assembly process between metal ions and ligands is known to depend on steric and interactive information stored in the ligand and governed by the metal ions through their coordination geometry demands.[1b,1c] Recently, a new type of aromaticity that results from the cyclical delocalization of electron density of d- as well as (d–p)π-type orbitals instead of the usual p orbitals on metal–ligand rings has been reported;[2] this may introduce greater stability to the higher-order structures. From this point of view, the ability of silver(I) thiolate or thionate complexes to adopt geometries with variable nuclearities and structural diversity makes the study of silver(I) chemistry very attractive.[3–4] Such silver(I) complexes with sulfur-containing ligands exhibit a wide range of applications in medicine, analytical chemistry, or the industrial preparation of polymers.[3,4] Biomedical applications and uses of silver(I) complexes are related to their antibacterial action,[5a,5b] which appears to involve interactions with DNA.[5c] The molecular design and structural characterization of silver(I) complexes is therefore an intriguing aspect of bioinorganic chemistry and metal-based drugs.[6]

A great deal of work has been devoted to the study of thioamides because of their tendency to bridge metal centers to form oligo- and polynuclear species with potential usage as functional solid materials.[7] Furthermore, 2-mercapto-3,4,5,6-tetrahydropyrimidine can coordinate up to three metal centers at short distances, which offers the possibility of studying the metal–metal interaction of d^{10} systems which have attracted considerable attention.[8] Such well-defined higher-order structures of 2-mercapto-3,4,5,6-tetrahydropyrimidine have already been reported for complexes **2** and **3**.[9]

In this paper, we report the structural and spectroscopic characterization of a new silver complex with the heterocyclic thioamide 2-mercapto-3,4,5,6-tetrahydropyrimidine (Scheme 1) of formula $\{[Ag_4Cl_4(\mu_3\text{-}StpmH_2)_4]_n\}$ (**1**). Also, a computational study of the aromaticity aimed at the rationalization of the stability of this structure and its ^{109}Ag NMR spectroscopic data in relation to the corresponding known complexes $\{[Ag_6(\mu_2\text{-}Br)_6(\mu_2\text{-}StpmH_2)_4(\mu_3\text{-}StpmH_2)_2]_n\}$ (**2**) and $\{[Ag_4(\mu_2\text{-}StpmH_2)_6](NO_3)_4\}_n$ (**3**) is de-

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tailed. To the best of our knowledge, this is the first example of an experimentally isolated silver(I) cluster that possesses (d-p)π-type quasiaromaticity.

Results and Discussion

General Aspects

The synthesis of complex **1** was carried out in DMSO with excess triethylamine according to the reaction shown in Equation (1).

$$4n\ \mathrm{AgCl} + 4n\ \mathrm{StpmtH_2} \xrightarrow[\mathrm{DMSO}]{\mathrm{Et_3N}} \{[\mathrm{Ag_4Cl_4}(\mu_3\text{-}\mathrm{StpmtH_2})_4]_n\} \quad (1)$$

No deprotonation of the thioamide ligand was observed in this case even though excess triethylamine was used. When 2-mercaptonicotinic acid reacted with silver(I) chloride under the same reaction conditions, a hexanuclear, water-soluble aggregate of formula $\{[Ag_6(\mu_3\text{-}Hmna)_4(\mu_3\text{-}mna)_2]^{2-}\cdot[(Et_3NH)^+]_2\cdot(DMSO)_2\cdot(H_2O)\}$ formed.[8d] Complex **1** has an infinite nanotube structure (vide infra) that consists of an octagonal Ag_4S_4 core. Four silver ions bridged by four sulfur atoms form an octagonal Ag_4S_4 core. Each Ag^I ion of a core is also bridged to a Ag^I ion of another core through a sulfur atom. Notably, the geometry around the silver(I) ions in **1** is tetrahedral.

The formula of synthesized compound **1** was first deduced from elemental analysis and spectroscopic data. Complex **1** is soluble in DMSO and DMF. The crystals of the complex were stable in air but were stored in darkness.

With the use of 3-(*tert*-butyldimethylsilyl)pyridine-2-thione, and 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione,[10a] 2-(triorganosilyl)thiophenols, 2,6-bis(triorganosilyl)thiophenols,[10b] and 2-(triorganosilyl)methanethione[10c] as ligands for the silver(I) ions, Zubieta et al.[10] established that the extent of the association in silver(I) ions in their clusters intimately depends on the nature of the thioamide. Thus, silver(I) ions with unbranched-chain thiolate ligands are highly polymeric as silver(I) is unprotected from the approach of additional bridging thiolate groups, whereas bulky ligands such as substituted thiolates increase the aggregation degree of the class of $[Ag(LS)]_n$ compounds.[10] In accordance with the above findings, the aggregate of formula $\{[Ag_6(\mu_3\text{-}Hmna)_4(\mu_3\text{-}mna)_2]^{2-}\cdot[(Et_3NH)^+]_2\cdot(DMSO)_2\cdot(H_2O)\}$[8d] was recently synthesized by using the branched substituted 2-mercaptonicotinic acid. When the unbranched, nonaromatic 2-mercapto-3,4,5,6-tetrahydropyrimidine was used for the synthesis of complexes **1**, $\{[Ag_6(\mu_2\text{-}Br)_6(\mu_2\text{-}StpmH_2)_4(\mu_3\text{-}StpmH_2)_2]_n\}$ (**2**),[9] and $\{[Ag_4(\mu_2\text{-}StpmH_2)_6](NO_3)_4\}_n$ (**3**),[9] highly polymeric structures, were obtained.

Spectroscopy

Infrared: The infrared spectra of complex **1** show distinct vibrational bands at 1572 and 1235 cm^{-1}, which were assigned as vibrations of the C–N bond (thioamide I and II bands), and at 1017 and 621 cm^{-1}, which were attributed to the C–S bond vibrations (thioamide III and IV bands). The corresponding thioamide bands of the free 2-mercapto-3,4,5,6-tetrahydropyrimidine ligand are given at 1557, 1206, 1067, and 644 cm^{-1}. The new band at 142 cm^{-1} in the far-IR spectrum of complex **1** was assigned to the vibration of the Ag–S bond,[11] whereas a band appearing at 149 cm^{-1} was attributed to the vibration of the Ag–Cl bond.

NMR: The ^{1}H NMR spectrum of a [D$_6$]DMSO solution of free ligand $StpmH_2$ shows resonance signals at δ = 7.86 ppm for the amide proton and at δ = 3.20 and 1.75 ppm for the CH_2 a and b protons. The band for the amide protons is shifted to 8.80 ppm in the ^{1}H NMR spectrum of complex **1**, obtained from a [D$_6$]DMSO solution, which confirms the N,S–metal coordination.

The ^{109}Ag NMR spectrum of complex **1** shows a signal at δ = +852 ppm. The corresponding signals for **2** and **3** are found at δ = 753 and 709 ppm, respectively. The significantly higher value of the chemical shift in the case of complex **1** relative to that of **2** and **3** could be due to the calculated aromaticity of complex **1** (see Computational Study). When the silver(I) ion is coordinated to the imine nitrogen atoms of a neutral N_4 donor system, as in the case of $[Ag_2\{\mu\text{-}(R,S)\text{-}1,2\text{-}(6\text{-}R\text{-}py\text{-}2\text{-}CH{=}N)_2Cy_2\}](OSCF_3)_2$ {where (R,S) = 1,2-(6-R-py-2-CH=N)$_2$Cy and R = H (a) or Me (b), and Cy = cyclohexane}, the chemical shift value for (a) is δ = 580 ppm and for (b) δ = 612 ppm.[12]

Crystal and Molecular Structures of Complex $\{[Ag_4Cl_4(\mu_3\text{-}StpmH_2)_4]_n\}$ (1)

In complex **1** (Figure 1), four μ_3-S atoms from the thione ligands bridge four silver(I) ions, which forms an eight-membered ring. The four Ag^I ions define an Ag_4 plane that rises 0.826 Å from the corresponding S_4 plane defined by the sulfur atoms. Strong μ_3-S intramolecular interactions bridge two eight-membered rings through silver(I) ions, whereas the coordination sphere of each silver ion is completed by a terminal Cl atom. The distance between two Ag_4 planes is 3.481 Å, which shows a stacking interaction. The same distance between two subsequent S_4 planes is also observed. Thus, an infinite nanotube structure is formed with strong interatomic interactions (Figure 2). A disordered solvent molecule (not identified) is also trapped inside the voids that are formed between the nanotubes.

The Ag–S bond lengths are Ag1–S2 = 2.5117(11) Å, Ag1–S2B = 2.5421(11) Å (symmetry code to equivalent position B: $1-y$, $-1+x$, z) and Ag1–S2A = 2.6627(13) Å (symmetry code to equivalent position A: x, $-y$, $z+1/2$). These values are in the range of those measured in complexes with infinite ribbon structures as in $\{[Ag_6(\mu_3\text{-}pyS)_4(\mu_4\text{-}pyS)_2]_n\}$[1a] [Ag–S = 2.456(5) to 2.959(5) Å], $\{[Ag_5(pyS)_4(pySH)BF_4]_n\}$[7] (Ag–S = 2.45 to 2.90 Å), $\{[Ag_6(SPh)_8](Me_4N)_2\}$[11] [Ag–S = 2.431(3) to 2.878(2) Å], and $\{[Ag(\mu_2\text{-}pyS)]_n\}$[1a] [Ag–S = 2.587(4) and Ag–S(a) = 2.502 Å] (pySH = 2-mercaptopyridine).

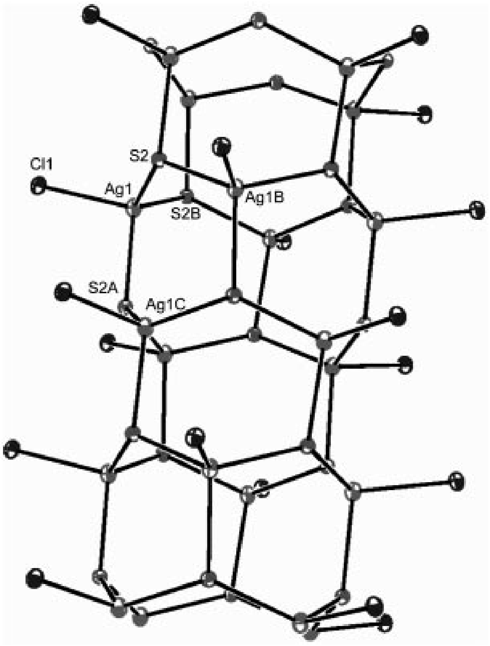


Figure 1. Molecular diagram of compound **1** together with the atomic numbering scheme (C, H, and N atoms were omitted for clarity). Symmetry codes to equivalent positions: A: 1 –*y*, –1 + *x*, *z*, B: *x*, –*y*, 1/2 + *z*, C: 1 –*y*, –1 + *x*, *z*. The displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: Ag1–S2 = 2.5117(11), Ag1–S2B = 2.5421(11), Ag1–S2A = 2.6627(13), Ag1–Cl1 = 2.6627(13), Ag1···Ag1B = 4.4614(5). Contact across ring [Å]: S2···S2A = 4.119(1), Ag1···Ag1C = 4.3487(5). Selected angles [°]; Cl1–Ag1–S2 = 109.04(4), Cl1–Ag1–S2B = 108.82(4), Cl1–Ag1–S2A = 101.41(4), S2–Ag1–S2B = 119.26(5), S2–Ag1–S2A = 112.18(3), S2B–Ag1–S2A = 104.61(3).

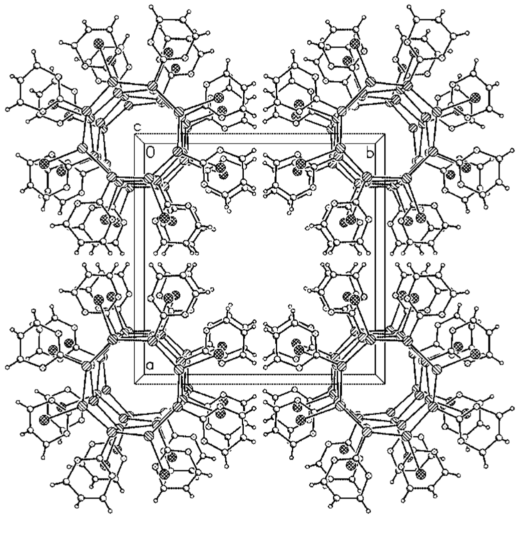
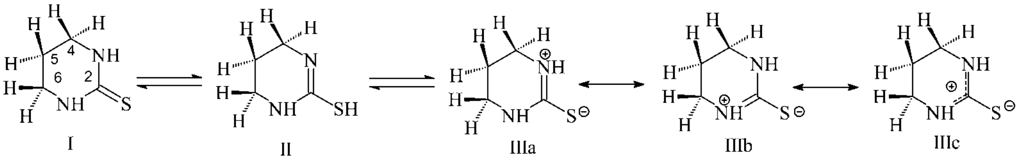


Figure 2. Unit cell of complex **1**. Strong μ_3-S bonding interaction between Ag^I ions of octagonal Ag_4S_4 cores lead to an infinite nanotube structure. The disordered guest molecule was omitted for clarity.

The Ag···Ag distance in the Ag_4S_4 ring in complex **1** is Ag1···Ag1B = 4.4614(5) Å, whereas the Ag···Ag distance between two subsequent rings is Ag1···Ag1C = 4.3487(5) Å (symmetry code to equivalent position C: 1 –*y*, –1 + *x*, *z*) and this is longer than twice the van der Waals radius for silver (3.44 Å),[6b] which indicates that there is no Ag···Ag interaction. The corresponding Ag···Ag distances in $\{[Ag_6(\mu_2\text{-}Br)_6(\mu_2\text{-}StpmH_2)_4(\mu_3\text{-}StpmH_2)_2]_n\}$ (**2**) are 3.063(1) Å and 2.963(2) Å, and they are shorter than twice the van der Waals radius for silver, which indicates that there is a strong Ag···Ag interaction, whereas in the case of complex $\{[Ag_4(\mu_2\text{-}StpmH_2)_6](NO_3)_4\}_n$ (**3**), no Ag···Ag interaction was observed because Ag1–Ag1B = 3.666(5) Å and Ag1–Ag1C = 3.954(5) Å. Other compounds presenting Ag···Ag interactions include $\{[Ag_6(\mu_3\text{-}pyS)_4(\mu_4\text{-}pyS)_2]_n\}$,[1a] with Ag···Ag = 2.959(2) Å, the neutral cluster $\{[Ag_6(\mu_3\text{-}Hmna)_6]\cdot 8DMSO\}$ (H_2mna = 2-mercaptonicotinic acid)[6b] with Ag···Ag = 2.911(1) Å, $\{[Ag_5(pyS)_4(pySH)BF_4]_n\}$[7] with Ag···Ag = 2.995 Å, $\{[Ag_6(\mu_3\text{-}Hmna)_4(\mu_3\text{-}mna)_2]^{2-}\cdot[(Et_3NH)^+]_2\cdot(DMSO)_2\cdot(H_2O)\}$[9] with Ag···Ag = 2.916 Å, and $\{[Ag_6(SPh)_8](Me_4N)_2\}$[11] with Ag···Ag = 2.959(1) Å. It is noteworthy that in all complexes with a short silver(I)–silver(I) distance (shorter than twice the van der Waals radius for silver) there is no halogen atom in the coordination sphere of the metal center. Complex **2** is still the only example of a silver(I) cluster containing a bromide ion in the coordination sphere of the metal center and presenting a Ag···Ag interaction.

The C–S bond length found in complex **1** is S2–C2 = 1.755(5) Å, which shows single bond character, whereas the C–N bond lengths are C2–N1 = 1.323(6) Å, C2–N3 = 1.328(5) Å, C6–N1 = 1.453(5) Å, and C4–N3 = 1.480(5) Å. Thus, in this case there are two equivalent short C–N bonds and a single C–S bond upon coordination to the silver(I) ion. These bond lengths, as well as all bond angles C–N–C and N–C–S that are around 122° [C2–N1–C6 = 123.7(4) and C2–N3–C4 = 121.8(4)°] and 119° [N1–C2–S2 = 119.9(3)° and N3–C2–S2 = 119.0(4)°], indicate that the ligand coordinates to silver(I) ion through zwitterionic form IIIc (Scheme 1).

The Ag–S–Ag bond angle in the Ag_4S_4 octagonal ring of complex **1** is S2–Ag1–S2B = 119.25(4)°, which is far from the ideal value of 135° of the normal octagon because of the nonplanar arrangements of the atoms, whereas the corresponding Ag–S–Ag angles formed between the octagonal



Scheme 1.

rings are S2–Ag1–S2A = 112.18(4)° and S2B–Ag1–S2A = 104.57(4)°.

Computational Study

Theoretical as well as experimental evidence of aromaticity in all-metal systems[13a] has introduced a novel category of compounds containing either an aromatic cycle completely composed of metal atoms[2c,2e,2f] or ligand-stabilized aromatic molecules with the ligands being either terminal or bridging adjacent metal atoms.[13b,13c] Furthermore, aromatic clusters involving d orbitals in pseudooctahedral and in tetrahedral three-dimensional metal cages were extensively studied by density functional methods.[2b,2e] Despite that, experimentally structurally characterized compounds containing aromatic metalloid and metal clusters play a significant role in the *metallaromaticity* concept because they verify results obtained computationally.[13d–13f] We evaluated the aromaticity of compound **1** by means of magnetic criteria and by utilizing the nucleus-independent chemical shifts (NICS) method proposed by Schleyer et al. in 1996[2a] as a precept to estimate the aromatic character of cyclic structures.

NICS indexes are defined as the negative isotropic values of the absolute magnetic shieldings calculated at the geometric ring centers (nonweighted mean of the heavy atom coordinates) and at the cage metal centers. In general, negative and positive NICS values are associated with aromatic and antiaromatic character, respectively, whereas values near zero are indicative of nonaromaticity. The use of the NICS method in 3D structures has been recently evaluated comprehensively[13g] showing the successful estimation of aromaticity. Here, the core of compound **1** adopts a D_4 symmetry and to assess its aromaticity we have calculated NICS values at the geometric cage center, NICS(0), and at various equal distances along the C_4 symmetry axis (Figure 3).

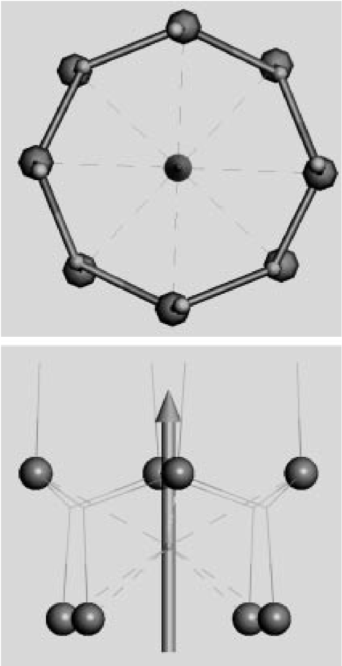


Figure 3. Geometrical representation for the core structure along and alongside the main symmetry axis.

The calculated results are illustrated in Figure 4, and they should be compared with the corresponding value of –6.9 ppm obtained for benzene at the same level of theory. The NICS data of –9.7 ppm at the cage barycenter confirms the aromatic character of the structure. The shielding influence reaches its minimum value of –13.1 ppm at NICS(1.7), which is the geometric center of one of the two D_{4h} four-membered metal rings, whereas NICS(–1.7) is –6.4 ppm. Both results suggest the presence of induced diatropic ring current at each of the molecular planes that is set up by four Ag and four S atoms,[13e] and it is this (d-p)π bonding that accounts for the equalization of the Ag–S bonds in the homometallic clusters. Also, induced diatropic ring current is characteristic of cyclic electron delocalization of d or (d-p)π-type orbital electron density,[13e] which causes the strong chemical shifts of the ^{109}Ag NMR signals in the spectrum of complex **1** (see NMR Study). Consistent with the literature,[13h] the sensitivity of NICS falls considerably with distance and the values are shifted downfield as the distance from the centre is increased, which eventually is proven as a suitable position for the evaluation of aromaticity.

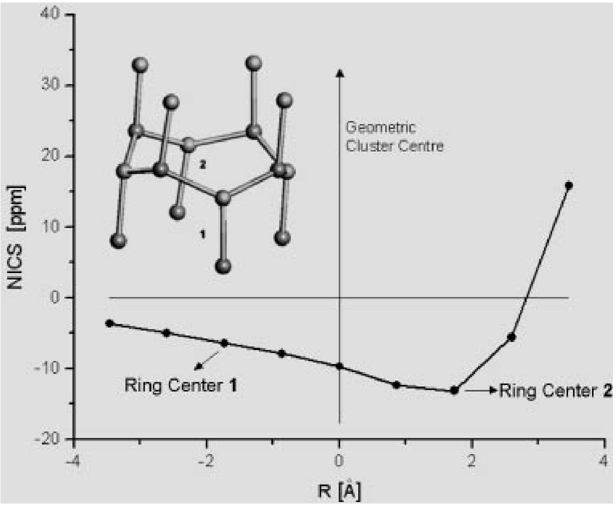


Figure 4. A plot of B3LYP/LANL2DZ NICS calculated along the C_4 axis for the asymmetric unit.

Conclusions

One new Ag^I aggregate was synthesized by the reaction of silver chloride and 2-mercapto-3,4,5,6-tetrahydropyrimidine. The crystal structure of complex **1** reveals that the formed Ag_4S_4 core exhibits strong (d-p)π-type quasiaromaticity. Stacking interactions between sequential rings are also observed. As a result, the ^{109}Ag NMR resonance signal of complex **1** is observed at a higher positive value relative to that observed for complexes **2** and **3**. Thus, the delocalization of the electron density in the (d-p)π-type orbitals, which results from quasiaromaticity, leads to deshielding of the electron density at the silver atoms.

Experimental Section

Materials and Instruments: All solvents were of reagent grade. 2-Mercapto-3,4,5,6-tetrahydropyrimidine (Aldrich) was used with no further purification. Elemental analyses for C, H, N, and S were carried out with a Carlo Erba EA model 1108 elemental analyzer. Infrared were recorded with a Perkin–Elmer Spectrum GX FTIR spectrophotometer. A Jasco UV/Vis/NIR V 570 series spectrophotometer was used to obtain the electronic absorption spectra. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 250 FTNMR instrument. Chemical shifts are given relative to internal tetramethylsilane. The ^{109}Ag NMR spectra were recorded with a Bruker DRX-600 spectrometer with Ag-109 resonance at 27.93 MHz at 30 °C, and $AgNO_3$ was used as a reference standard.

Synthesis and Crystallization of $\{[Ag_4Cl_4(\mu_3\text{-StpmH}_2)_4]_n\}$ (1): A clear DMSO solution (7 mL) of 2-mercapto-3,4,5,6-tetrahydropyrimidine (0.234 g, 2 mmol) was treated with silver(I) chloride (0.143 g, 1 mmol). After stirring for 30 min, triethylamine (0.5 mL, 3.6 mmol) was added. The resulting clear solution was then filtered, and the filtrate was kept in the dark at room temp. After a few days, colorless crystals (0.10 × 0.20 × 0.30 mm) of complex **1** that were suitable for single-crystal X-ray analysis were obtained. M.p. 190–195 °C. ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 8.80 (s, 1 H, NH), 3.40 (t, 2 H, J = 7 Hz, C^4H_2), 1.81 (q, J = 7 Hz, 2 H, C^5H_2) ppm. IR (KBr): $\tilde{\nu}$ = 3199, 1572, 1235, 1017, 621 cm^{-1}. Far-IR (polyethylene): $\tilde{\nu}$ = 142, 149 cm^{-1}. UV/Vis (DMSO): λ = 258.0 nm. $C_4H_8AgClN_2S$: calcd. C 18.51, H 3.11, N 10.79, S 12.36; found C 18.89, H 2.97, N 10.95, S 12.22.

Computational Details: Calculations were based on the molecular geometry acquired by X-ray diffraction methods. Magnetic shielding tensors for a ghost atom placed at different interior and near exterior positions of the metal–ligand cluster (asymmetric unit) were computed by using the gauge-independent atomic orbital (GIAO) DFT method[14a–14c] within the B3LYP level of theory. Nucleus independent chemical shift (NICS) values were estimated with the B3LYP functional by using the Los Alamos effective core potentials plus double zeta (LANL2DZ).[14d] All theoretical results reported were carried out with the Gaussian03W program package.[14e]

X-ray Structure Determination: Data were collected by the ω scan technique in the range 3.9° $< 2\theta <$ 29.1° with a KUMA KM4CCD four-circle diffractometer[15a] equipped with a CCD detector with the use of graphite-monochromated Mo-K_α (λ = 0.71073 Å) at 100(1) K. Cell parameters were determined by a least-squares fit method.[15b] All data were corrected for Lorentz-polarization effects and absorption.[15b,15c] The structure was solved with direct methods with SHELXS97[15d] and refined by full-matrix least-squares procedure on F^2 with SHELXL97.[15e] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located at calculated positions and refined as a "riding model" with isotropic thermal parameters fixed at 1.2 times the U_{eq}'s of the appropriate carrier atom.

1: $C_4H_8AgN_2S$, tetragonal in $P4cc$, a = 15.7761(9) Å, b = 15.7761(9) Å, c = 6.9624(8) Å, V = 1732.8(2) Å^3, Z = 2, T = 100(1) K, $\rho_{calcd.}$ = 2.166 g cm^{-3}, μ = 2.8 mm^{-1}, reflections collected: total, unique data, R(int) = 9927, 1824, 0.043, index range: $-21 < h < 20$, $-21 < k < 20$, $-9 < l < 7$, observed data [$I > 2.0$ sigma(I)]: 1445, final $R^{[a]}$, $wR2^{[b]}$ [$I > 2\sigma(I)$] indices: 0.0289 and 0.0605, respectively. ([a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$), goodness of fit: 1.032.

CCDC-624697 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The graduate program in Bioinorganic Chemistry financed by the Ministry of Education of Greece and coordinated by Professor N. Hadjiliadis is acknowledged. N. H. and I. S. also thank a NATO grant for exchange of scientists that they were awarded.

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Received: December 13, 2006