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Synthesis and Photophysical Study of an Octahedral Silver(I) 1-D Coordination Polymer with Thiocarboxylic-Acid-Based Ligands

Ume Farwa,^{a,1} Moumita Pait,^{a,1} Ji Yeon Ryu,^a Sunwoo Lee,^a Youngjo Kim, ^{*, b} Hyoung-Ryun Park,^{*,a} and Junseong Lee^{*,a}

^a Department of Chemistry, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Republic of Korea. Fax: 82 62 530 3389; Tel: 82 62 530 3371; E-mail: hrpark@chonnam.ac.kr, leespy@chonnam.ac.kr

^b Department of Chemistry and BK21+ Program Research Team, Chungbuk National University, Cheongju, Chungbuk 361-763, Republic of Korea

E-mail: ykim@chungbuk.ac.kr

¹These authors have contributed equally.

Abstract

We describe the synthesis of a unique 1-D silver coordination polymer, in which the silver center is, unusually, six-coordinate. The reaction of 2,3,5,6-tetrakismetal (carboxymethylthio)-benzenediol (H_2L) and $AgNO_3$ in a 1:2 molar ratio resulted in the esterification of the carboxylic acid groups and the oxidation of quinol to quinone. As a result, a methylesterthioquinone ligand (L^1) was obtained. By increasing the molar ratio of Ag to four equivalents, a 1-D coordination polymer, $[AgL^{1}(NO_{3})]_{n}$ (1), was obtained. The simple reaction of L^1 and AgNO₃ in a 1:2 molar ratio also produced complex 1 in quantitative yield. Both the esterified ligand L^1 and the coordination polymer 1 were fully characterized by infrared and ¹H NMR spectroscopy, elemental analysis, electrospray ionization mass spectrometry, and single crystal X-ray crystallography. The single crystal X-ray diffraction measurements revealed that the Ag metal center has an octahedral geometry with η^2 -nitrate ligands. The photophysical properties of complexes are also explored.

Keywords: Silver • Thiocarboxyl • 1-D • Coordination polymer • Octahedral coordination

CCEN

Introduction

Interest in the development of molecular electronic devices [1]–[2] and redox substances has increased. For this purpose, coordination polymers (CP's) of d¹⁰ metal complexes have attracted significant interest. These CP's not only offer diverse topologies and remarkable structural features but also have applications in sensing [3-8], gas storage [9-17], selective heterogeneous catalysis [18-25], and magnetic devices [26-32]. In CP's, the molecular electronic characteristics of the ligands in combination with the coordination geometry of the metal yield unique properties.

There are various factors controlling the synthesis of CP's, such as the metal/ligand ratio, concentration, temperature, and type of counterion used. However, the choice of metal and the design of the ligand are the most important factors. Ag is widely employed for the construction of CP's because its CP's have flexible geometries, variable coordination numbers, π interactions, and unusual electronic and photophysical characteristics [6, 33-46]. To date, various multidentate organic ligands have been synthesized with different properties. Sulfur-containing compounds, such as aromatic poly(phenylthio) ligands, have been explored because of their electron-accepting and delocalizing electrochemical properties [2]. Many thio-substituted benzene ligands have been studied for the construction of Ag(I) CP's. The soft nature of sulfur-containing ligands and silver results in interesting combinations for the design of CP's [47, 48].

In this work, we used a thiocarboxylic acid based ligand, 2,3,5,6-tetrakis-(carboxymethylthio)-benzenediol, and studied its reactions with silver salts. In our work, we found that the metal to ligand ratio is very important for the synthesis of the 1-D coordination polymer. The use of ligand H_2L with two equivalents of AgNO₃ in MeOH led to the oxidation of the quinol ligand to quinone with the simultaneous esterification of the carboxylic acid groups present in the ligand. The reaction of AgNO₃ and the ligand in a 4:1 molar ratio in MeOH resulted in the formation of dark red crystals of a nitrate-bridged Ag^I coordination polymer. In this crystal, the geometry of silver metal center is octahedral, which is very unusual [49]. Furthermore, we explored the photophysical properties of the octahedral silver(I) 1-D coordination polymer.

Results and Discussion

Synthesis and Characterization

The synthesis of our target molecule was achieved as shown in Scheme 1. The quinol ligand (2,4,5-tris-carboxymethylsulfanyl-3,6-dihydroxy-phenylsulfanyl)-acetic acid (H₂L)was synthesized following a literature procedure [50], and its reactions with Ag^I salts were methodically explored to obtain the ligand L^1 and coordination polymer AgL¹ (Scheme 1). The reaction of ligand H_2L in MeOH with two equivalents of AgNO₃ at 60 °C led to the oxidation of the quinol ligand to quinone with the simultaneous esterification of the carboxylate groups present in the ligand. The new ligand, L^1 , crystallized overnight directly from the reaction mixture as a red solid suitable for X-ray analysis. The yield was ~46%. Subsequently, we repeated the reaction with an excess of AgNO₃ compared to the previous reactions. The reaction of AgNO₃ and the ligand in 4:1 molar ratio in MeOH at 60 °C produced a reddish-brown solution and an ivory-colored powder. Dark-red crystals of nitratebridged Ag^I coordination polymer (Scheme 1) were identified as the major product in ~42% yield. In these reaction systems, two equivalents of $AgNO_3$ were used for the oxidation of quinol to quinone, and the remaining two equivalents of AgNO₃ participated in the formation of the complex. The reaction of AgNO₃ and L^1 in a molar ratio of 2:1 also produced the desired product, 1. We further tried the reaction with excess AgNO₃; however, we have failed to isolate any characterizable product. Various synthetic conditions and reaction systems were explored with different stoichiometries before a reproducible synthetic procedure was established.



Scheme 1. Synthesis of quinone ligand L^1 and complex AgL^1 .

Characteristic bands of the two ligands and the complex are present in the Fourier transform infrared (FT-IR) spectra. The $\bar{\nu}_{OH}$ and $\bar{\nu}_{COOH}$ stretching frequencies for ligand H₂L appear at 3304–3100 cm⁻¹. The $\bar{\nu}_{COOMe}$ stretching frequencies appear at 1735 and 1737

cm⁻¹ for ligand \mathbf{L}^1 and the **Ag-L**¹ complex, respectively. For **Ag-L**¹ a very strong characteristic band at 1384 cm⁻¹ is attributed to the $v_3(E')$ mode of the NO₃⁻ group.

The ¹H NMR spectra of L^1 shows two sets of peaks that can be attributed to the presence of quinone forms in solution. The peaks at 3.717 and 3.561 ppm can be assigned to the $-CH_2$ and $-CH_3$ protons of the quinone form of the ligand. The ¹H NMR results of the Ag- L^1 crystal also shows that only single complex is present in solution. The use of higher molar ratio AgNO₃ not only resulted in the complexation of Ag and L¹ but also complete oxidation of quinol to quinone.

Solid State Structures.

The esterified ligand L^1 crystallizes in the monoclinic space group $P2_1/c$.(Figure 1) The crystal structure of ligand L^1 shows that the thiocarbonyl acid has been esterified and the quinol group has been converted to quinone. Unlike the solution state ¹H NMR results, which indicate that both quinone and quinol are present in solution, the solid product contains only the quinone form. This indicates that the quinone form of L^1 is more energetically stable and precipitates preferentially. The crystal structure shows that two of the four methylthioester arms are directed inward, while the other two are directed outward. The bond angles between the sulfur atoms and benzene carbon atoms range from 101.7(2)° to 104.6(2)° (Figure 1a).





Figure 1. Crystal structure of ligand L^1 : (a) Top view, (b) side view. Hydrogen atoms have been omitted for clarity. Colors: S, yellow; O, red; C, black.

The $[AgL^{1}(NO_{3})]_{n}$ CP crystallizes in the monoclinic space group $P2_{1}/n$. The asymmetric unit of the complex consists of a ligand molecule, a silver atom, and a nitrate ion (Figure 2a). The Ag atom is coordinated by six atoms, four S atoms from two molecules of L^{1} and two O from the nitrate ion, thus exhibiting an octahedral geometry with bond angles around the Ag(1) cation ranging from 51.8(3)° to 141.4(7)°. The coordination of Ag¹ with the thioester group of the ligand rather than the O from the quinone group present at the para position agrees well with the "hard and soft acids and bases" (HSAB) theory. Interestingly, the Ag center in this crystal has a rare octahedral geometry. The silver center is bonded to two S atoms from the ligand and two oxygen atoms from nitrate ion. Figure 2b shows the helical 1D coordination polymer chain for the Ag-L¹. The additional S…S (green dotted line) and S…O (pink dotted line) interactions assemble units of 1 into sheets in the (010) plane (Figure 2c-d). Additional weak CH…O interactions (Figure 2e) result in a 3-D network structure (Figure 2(e). The η^{2} nitrate does not participate in the extended chains.

In order to investigate the bulk properties of L^1 and complex 1, TGA experiments were conducted and the thermograms were obtained as shown in Figure s7 and s8. The thermal degradation of L^1 consist of three weight loss steps, where the first and second weight loss below 350 °C could be ascribed to partial decomposition of ester groups. The third weight loss could be attributed to the thermal decomposition of the remaining sulfur and quinone

part. The thermal degradation of **1** provides more complicated five step weigh loss. The first weight loss below 150 °C seems to be the evaporation of solvents. The second, third and forth weight loss steps could be attributed to the thermal decomposition of the ester groups and remaining organic parts, respectively.



(**b**) 1-D extended view along the *c*-axis.





(f) 3-D extended view in the (101) plane.

Figure 2. Crystal structure of (a) the asymmetric unit of complex **1** with selected atomnumbering scheme, (b) 1-D extended view along the *c*-axis, (c) connectivity of complex **1** in the (010) plane, (d) connectivity of complex **1** in the (101) plane, (e) 2-D extended view in the *ac*-plane, and (f) 3-D extended view in the (101) plane. Hydrogen atoms have been omitted for clarity. Colors: Ag, light gray; N, blue; O, red; C, gray. Selected bond lengths (Å) and angles (deg): Ag1–S1 2.663(2), Ag1–S2 2.778(2), Ag1–S3 2.693(2), Ag1–S4 2.763(2), Ag1–O11 2.417(7), Ag1–O12 2.487(6), O1–C1 1.207(8), O2–C4, S1–Ag1–S2 74.58(6),

S2-Ag1-S3 90.70(7), O11-Ag1-O12 51.8(3), S1-Ag1-O11 93.8(2), S3-Ag1-O12 88.92(17), S1-Ag1-S4 92.95(7), S3-Ag1-S4 73.38(6), S2-Ag1-O11 114.7(2), S2-Ag1-O12 87.4(2).

UV-Vis Spectra

To investigate the photophyscial properties of complexes, UV-Vis spectra were obtained. (Figure 3) In the spectrum of ligand H₂L, the absorption maximum peaks (λ_{max}) are found at 244 and 351 nm, having molar extinction coefficients of 67500 and 16300 M⁻¹cm⁻¹, respectively (Table 1). These values can be attributed to the π - π * and n- π * electronic transitions taking place in H₂L. The esterified ligand, L¹, which has a quinone group, has λ_{max} values at 228 and 370 nm, and the molar extinction coefficient values for L¹ are 46300 and 30100 M⁻¹cm⁻¹, respectively. The λ_{max} at 228 nm shows a hypsochromic shift of 16 nm with a decrease in the absorption intensity compared to that of H₂L. The value of λ_{max} at 370 nm shows a bathochromic shift of 19 nm with an increase in the absorption intensity in comparison with that of H₂L. The shift of λ_{max} and change in absorption intensities can be attributed to the new structural features in L¹ [51], that is, the change of functional group from an acid to ester group and the oxidation of quinol to quinone.

In the spectrum of Ag- L^1 , λ_{max} are found at 211 and 378 nm, and the molar extinction coefficients are 29500 and 12500 M⁻¹cm⁻¹, respectively. These values indicate an inter-ligand electronic transition [52], i.e., π - π * and n- π *. The absorption maxima of Ag- L^1 show a hypsochromic shift of 17 nm and a bathochromic shift of 8 nm compared to those of L^1 . In contrast, there is a clear decrease in the absorption intensity of the Ag- L^1 spectra as compared to that of L^1 . This could be because, in the solution state, L^1 contains both quinone and unoxidized quinol forms, as shown by NMR. However, in the case of complex 1, only the quinone form of the ligand is present.

Sample	λ_{\max} (nm)	$\mathcal{E}(\mathbf{M}^{-1}\mathbf{cm}^{-1})$
$H_2 L$	244	67500
	351	16300
L^1	228	46300
	370	30100

Table 1. Comparison of the absorption maxima of the complexes.



Figure 3. UV-Vis spectra of H_2L , L_1 and complex 1.

Conclusion

In this paper, we demonstrated that by using a 1:2 molar ratio of (H_2L) and AgNO₃, the carboxylic acid group can be esterified and the quinol can be oxidized to a quinone, resulting in the isolation of crystals of the methylesterthioquinone ligand (L^1) . We further doubled the molar ratio of AgNO₃, and, surprisingly, a 1-D coordination polymer, $[AgL^1(NO_3)]_n$ was obtained. Unlike the typical low coordination numbers and related geometries of silver coordination compounds, the Ag center was found to have an octahedral geometry. Furthermore photphysical properties of (H_2L) , (L^1) and complex 1 were investigated. The results dictate that inter-ligand electronic transition takes place in complex 1 when exposed to UV-visible light.

Experimental Section

General Considerations. All experimental manipulations were carried out in air. The chemicals and solvents were reagent grade materials and used as received without further purification. The ¹H NMR and ¹³C spectra were recorded in DMSO- d_6 using a Bruker Advance 300 NMR spectrometer at 300.13 MHz and 75.47 MHz, respectively, at KBSI Gwangju. The IR spectra were recorded on a Bruker Tensor 27 equipped with an attenuated total reflectance (ATR) Harricks apparatus. Thermogravimetric analysis (TGA) measurements were performed in a nitrogen atmosphere using a mettler toledo TGA/DSC instrument with star system at a scanning rate of 10 °C /min.

Synthesis

Ligand H₂L. The ligand was prepared following a modified literature procedure [50]. *p*-Benzoquinone (2g, 20 mmol) was placed in 10 mL of water, and thioglycolic acid (5.41 mL, 80 mmol) in water was added very slowly, as mentioned in the literature, over 30 min. Immediately after the complete addition of thioglycolic acid, the brown solution became white. The product, a white powder, was obtained and separated by filtration and recrystallized from hot water. Yield 56%, IR peaks: 3340 (br), 1701 (s), 1431 (m), 1382 (m), 1310 (m), 1198 (m), 865 (w). ¹H NMR DMSO-*d*₆: 3.72 (s, -CH₂).

Ligand L¹. Ligand H₂L (47.05 mg, 0.1 mmol), silver nitrate (34 mg, 0.2 mmol), and MeOH (5mL) were charged into a 50-mL round bottom flask. The color of the reaction mixture became ivory. The reaction mixture was refluxed at 60 °C for 6 h. A blood red solution formed along with white colored ppt. The solution was filtered and left to slowly evaporate by ether diffusion. Red block-shaped single crystals were obtained overnight in moderate yield. Anal. Calc. for $C_{18}H_{20}O_{10}S_4$ C, 41.21; H, 3.84. Found: C, 40.82; H, 4.06. IR peaks (cm⁻¹): 3433 (br), 1735 (s), 1667 (m), 1435 (s), 1284 (s), 1173 (m), 1108 (m). ¹H NMR DMSO-*d*₆ (ppm): δ = 3.72 (s, -CH₃), 3.56 (s, -CH₂). ¹³C NMR DMSO-*d*₆ (ppm): δ = 172.72, 169.15, 125.91, 52.37, 34.36.

Complex AgL¹. Ligand H₂L (47.05 mg, 0.1 mmol), silver nitrate (68 mg, 0.4 mmol) and MeOH (5mL) were charged into a 50-mL round bottom flask, and the reaction was carried out as mentioned above. A reddish brown solution was formed with an ivory colored precipitate. Maroon needle-like crystals suitable for X-ray analysis were obtained by the slow

evaporation of the mother liquor overnight with moderate yield. Anal. Calc. for $C_{18}H_{20}O_{10}S_4$ (524.61) C, 31.13; H, 2.90. Found: C, 30.85; H, 2.53. Selected IR peaks (cm⁻¹): 3438 (br), 1737 (s), 1662 (m), 1384 (s) (nitrate group), 1301 (m), 1108 (m). ¹H NMR DMSO-*d*₆ (ppm): δ 3.93 (s, -CH₃), 3.66 (s, -CH₂). ESI-MS: *m/z* calcd for [**1**-NO₃]⁺: 630.90, found 632.84.

Physical Measurements. Elemental analyses (CHN) were performed with a Perkin-Elmer model 240C elemental analyzer. FT-IR spectra were recorded on a Perkin-Elmer 883 spectrometer. A solute concentration of 10⁻³ M was used, and a Shimadzu UV 3100 UV-vis-NIR spectrophotometer was used to record the electronic absorption spectra.

X-ray Crystallography. Suitable single crystals of **L** and **Ag-L** were examined using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75-kW sealed-tube Mo-K_{α} radiation generator (λ) 0.71073 Å. The data were collected at 298 K, by scanning ω in steps of 0.3° at a scan speed of 5 s per frame. The APEX2 software was used for data acquisition and data integration and reduction [53]. Structures were solved by direct methods using SHELXS-2014 and refined with full-matrix least squares on F^2 using SHELXL-2014 [54]. The locations of the heaviest atoms (Ag) were easily determined, and the O, N, and C atoms were subsequently determined from the difference Fourier maps. The non-H atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometries and riding thermal parameters with respect to their carrier atoms. A summary of the crystal data and relevant refinement parameters are given in Table 2.

Compound	L^1	1
CCDC #	1555905	1555906
Formula	$C_{18}H_{20}O_{10}S_4$	$C_{18}H_{20}AgNO_{13}S_4$
Formula weight	524.58	694.46
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	8.7253(4)	16.932(6)
b (Å)	31.2090(14)	9.380(3)
<i>c</i> (Å)	9.1641(4)	16.978(6)
α (°)	90	90
β (°)	109.945(2)	114.005(18)
γ (°)	90	90
V (Å3)	2345.78(18)	2463.4(15)
Ζ	4	4
$\rho_{calc} (g \text{ cm}^{-3})$	1.485	1.872
μ (mm ⁻¹)	0.456	1.226
F(000)	1088	1400
<i>T</i> (K)	296	100
Scan mode	ω and ϕ	ω and ϕ
	-10 <=h<=10,	-20 <=h<= +16,
<i>hkl</i> range	-36 <=k<= +36,	-9 <= k <= +10,
	-11 <=l<= +11	-16 <=1<= +20
Measured reflns	27431	11001
Unique reflns [<i>R</i> _{int}]	4381 [0.0814]	4225 [0.0766]
Reflns used for refinement	2410	3173
Refined parameters	293	339
$R_{1a} \left(I > 2\sigma(I) \right)$	0.0615	0.0446
wR_{2b} all data	0.1443	0.1044
GOF on F^2	0.995	1.008
ρ _{fin} (max/min) (eÅ ⁻³)	0.642, -0.382	0.758, -0.570

Table 2. Crystallographic data and parameters for L^1 and compound 1.

Supplementary Material

Mass spectrometry data, spectroscopic data and crystallographic data in CIF format are available in the Supporting Information. CCDC 1555905 and 1555906 contain supplementary crystallographic data for ligand L^1 and complex 1, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Pictograms



Synopsis: Whereas the reaction of 2,3,5,6-tetrakis-(carboxymethylthio)-benzenediol (H_2L) and $AgNO_3$ in a 1:2 molar ratio resulted in the esterification of the carboxylic acid groups and the oxidation of quinol to quinone, the reaction in a 1:4 molar ratio produced a 1-D coordination polymer, $[AgL^1(NO_3)]_n$.