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Synthesis, structural characterization, and crystal structure of bis(triphenylsulfonium)tetrachlorocuprate(II)

Grace Bennett , Kennedy Gaines , Morgan Barry , Mark Gillican ,
 Clifford Padgett , and Will Lynch  *

Department of Biochemistry, Chemistry and Physics, Faculty of the Center for Advanced Materials Science, Georgia Southern University, Savannah, Georgia, 31419, United States of America

* Corresponding author at: Department of Biochemistry, Chemistry and Physics, Faculty of the Center for Advanced Materials Science, Georgia Southern University, Savannah, Georgia, 31419, United States of America.
 e-mail: wlynch@georgiasouthern.edu (W. Lynch).

RESEARCH ARTICLE



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ABSTRACT

The synthesis and crystal structure of bis(triphenylsulfonium)tetrachlorocuprate(II) are reported. Single-crystal X-ray diffraction analysis revealed that the compound crystallizes in the monoclinic crystal system, space group Pn , with unit-cell parameters $a = 10.4463(1)$ Å, $b = 10.0143(1)$ Å, $c = 16.0734(1)$ Å, $\beta = 99.090(1)^\circ$, $V = 1660.36(3)$ Å³, and $Z = 2$. The asymmetric unit consists of two crystallographically independent triphenylsulfonium cations and one tetrachlorocuprate(II) anion. Both sulfonium centers adopt distorted trigonal-pyramidal geometries, with S-C bond lengths ranging from 1.779(4) to 1.792(4) Å and C-S-C bond angles between 103.6(2) and 105.40(19)°. The $[\text{CuCl}_4]^{2-}$ anion exhibits a significantly distorted tetrahedral geometry characterized by Cu-Cl bond lengths of 2.2364(13)-2.2723(11) Å, Cl-Cu-Cl bond angles of 96.15(5)-139.70(5)°, and a τ_4 value of 0.59, indicative of a flattened tetrahedral (seesaw-like) coordination environment. The observed structural parameters are consistent with those reported for related triphenylsulfonium and tetrachlorocuprate(II) salts, confirming the characteristic distortion of the $[\text{CuCl}_4]^{2-}$ unit in this class of compounds.

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1. Introduction

Aryl sulfonium salts are versatile organosulfur compounds and are widely used in a number of applications [1-3]. Recently, diphenyl(trifluoromethyl)sulfonium triflate has been reported to be an excellent electrophilic trifluoromethylation reagent [4]. Nonfluorinated alkyl(aryl) and triarylsulfonium salts have also been shown to be prevalent in arylation processes [5]. Sulfonium salts have also recently been reported for their utility in anion exchange membranes (AEMs) [6]. These materials have been found to have enhanced long-term stability compared to those of other AEM materials. This stability can be further enhanced by deploying sterically demanding aryl sulfonium salts that resist decomposition and oxidation [7].

Other reports include the utility of triphenylsulfonium (TPS) salts as photo-initiators in resin polymerization. This is a function of photolysis, proton release, and C-S bond scission [8]. This proton release has also been exploited in the use of TPS salts as photoacid generators, which have found applications in semiconductor synthesis [9] and exciton emission applications [10].

In this study, we report on the synthesis, crystal growth, and single-crystal structure determination of the complex salt triphenylsulfonium tetrachlorocuprate(II). This complex is formulated as $[\text{C}_{18}\text{H}_{15}\text{S}]_2[\text{CuCl}_4]$. This structure complements other examples from our laboratory in which the metal center is found in a tetrahedral environment and the sulfonium cations are trigonal pyramidal [11-13].

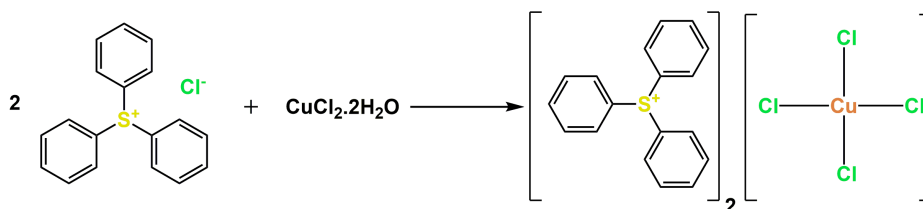
2. Experimental

2.1. Synthesis of bis(triphenylsulfonium)tetrachlorocuprate(II) [(TPS)₂][CuCl₄]

Triphenylsulfonium chloride (Millipore/Aldrich) (0.100 g, 0.335 mmol) was dissolved in 10 mL of methanol. Copper(II) chloride dihydrate (Millipore/Aldrich) (0.0285 g, 0.167 mmol) was added in one portion. The solution was stirred for 10 minutes to dissolve the copper salt. The solution was covered with parafilm and allowed to evaporate at room temperature to give yellow crystals (Scheme 1). Yield (0.0168 g, 13.9%)

Table 1. Crystal data and details of the structure refinement for [TPS]₂[CuCl₄].

Empirical formula	C ₃₆ H ₁₃₀ S ₂ Cl ₄ Cu
Formula weight (g/mol)	732.06
Temperature (K)	296
Crystal habit	Irregular, yellow
Crystal system	Monoclinic
Space group	<i>Pn</i>
<i>a</i> (Å)	10.4463 (1)
<i>b</i> (Å)	10.0143 (1)
<i>c</i> (Å)	16.0734 (1)
β (°)	99.090 (1)
<i>V</i> (Å ³)	1660.36 (3)
<i>Z</i>	2
<i>D_x</i> (Mg m ⁻³)	1.464
<i>M</i> (mm ⁻¹)	5.26
<i>F</i> (000)	750
Crystal size (mm ³)	0.18 × 0.16 × 0.16
Radiation	Cu K α radiation, λ = 1.54184 Å
2 θ Range for data collection	θ_{max} = 69.7°, θ_{min} = 4.4°
Index ranges	<i>h</i> = -12→12, <i>k</i> = -12→8, <i>l</i> = -18→19
Reflections collected	17754 measured reflections
Reflections (<i>I</i> > 2 σ (<i>I</i>))	5122 reflections
Independent reflections	5339 independent reflections
Goodness of fit on <i>F</i> ²	1.04
Final <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.030
w <i>R</i> (<i>F</i> ²)	0.078
Largest difference peak (e Å ⁻³)	0.25, -0.24

**Scheme 1.** Synthesis pathway of the title compound, bis(triphenylsulfonium) tetrachlorocuprate(II).

Selected FT-IR bands (ATR-IR, ν , cm⁻¹): 3023 (w), 1475 (s), 1446 (s), 1292 (s), 1069 (m), 995 (m), 773 (s), 747 (s), 683 (s), 498 (s).

2.2. Instrumentation

Infrared spectra were recorded on a PerkinElmer Spectrum-100 FT-IR instrument using ATR under ambient conditions.

2.3. Crystal structure determination and refinement

X-ray intensity data of 17,754 reflections (of which 5339 were independent and 5122 were observed) were collected on a Rigaku XtaLAB Synergy-S instrument with a HyPix3000 detector diffractometer equipped with graphite monochromated Cu K α radiation (λ = 1.54184 Å). The crystal used for data collection was of dimensions 0.18 × 0.16 × 0.16 mm. The cell dimensions were determined by the least-squares fit of the angular settings of 13,498 reflections in the θ range 2.8 to 69.4°. The intensities were measured using ω scans for θ ranges 4.4 to 69.7°. 5,122 reflections were treated as observed (*I* > 2 σ (*I*)). Data were corrected for Lorentz, polarization, and absorption factors. The structure was solved by direct methods using SHELXT [14]. All H atoms were geometrically fixed and allowed to ride on their parent C atoms with C-H = 0.93-0.98 Å. Full-matrix least squares refinement was carried out using SHELXL9 [15]. The final refinement cycles converged to an *R* = 0.0297 and w*R*(*F*²) = 0.0777 for the observed data. Residual electron densities ranged from -0.24 to 0.25 e.Å⁻³. The crystallographic data for the title compound are summarized in Table 1.

3. Results and discussion

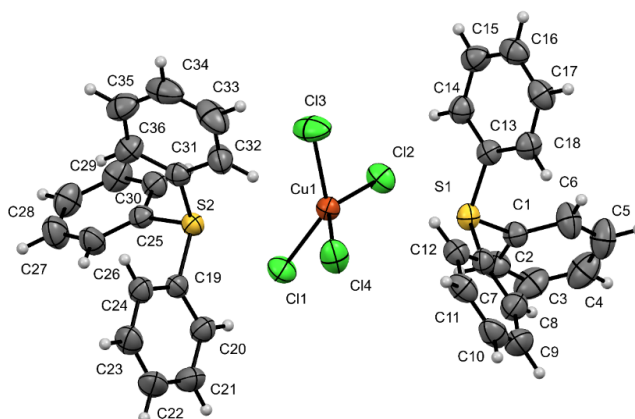
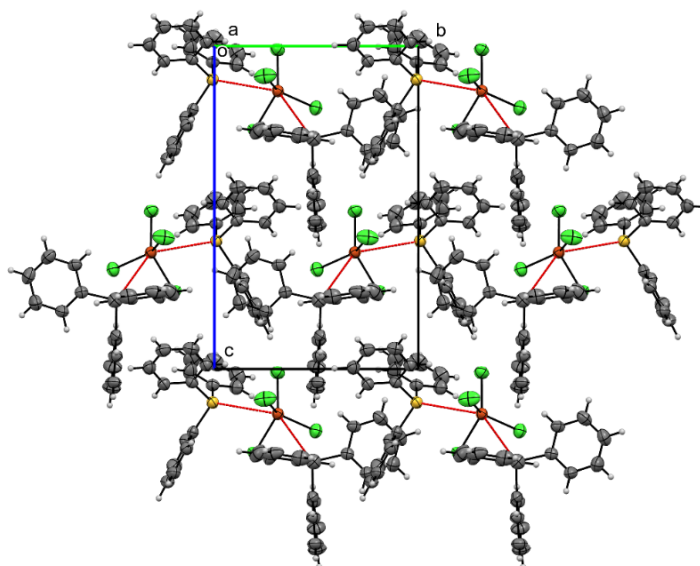
The title compound was synthesized in a straightforward manner by dissolving triphenylsulfonium chloride in methanol and adding copper(II) chloride dihydrate in one portion as shown in Scheme 1. The solution was stirred for 10 min and then slowly evaporated at room temperature, yielding X-ray quality crystals of the product. FT-IR spectroscopy supported the presence of the TPS cation in the complex with aromatic C-H stretch found at 3023 (w) cm⁻¹ and aromatic C=C stretches assigned to 1475 (s) cm⁻¹ and 1446 (s) cm⁻¹, while the lower frequency bands are assigned to C-H vibrations.

The crystal structure consists of two triphenylsulfonium cations and the tetrachlorocuprate(II) ion (Figure 1). [TPS]₂[CuCl₄] crystallizes in the monoclinic space group *Pn* and crystallographic data are given in Table 1. The asymmetric unit of [TPS]₂[CuCl₄] comprises two crystallographically independent C₁₈H₁₅S⁺ triphenylsulfonium (TPS⁺) cations and one [CuCl₄]²⁻ tetrachlorocuprate(II) anion.

Each sulfonium center exhibits a distorted trigonal-pyramidal geometry. In the first cation (containing S1), the S-C bond lengths range from 1.780(4) to 1.792(4) Å, while the C-S-C angles span 103.6(2)-104.97(19)°. In the second cation (containing S2), the S-C distances lie between 1.779(4) and 1.789(4) Å, and the C-S-C angles vary from 103.66(19) to 105.40(19)°. The C31-S2-C19 bond angle is wider by >1.4° than the other two C-S-C bond angles in the S2 cation. The tetrachlorocuprate(II) anion, [CuCl₄]²⁻, adopts a distorted tetrahedral geometry with a τ_4 value of 0.59 [16]. The Cu-Cl bond lengths are in the range 2.2364(13)-2.2723(11) Å, while Cl-Cu-Cl bond angles span 96.15(5)° for Cl1-Cu1-Cl4 to 139.70(5)° for Cl4-Cu1-Cl2, indicating significant distortion from ideal tetrahedral geometry.

Table 2. Bond lengths of the [TPS]₂[CuCl₄] complex.

Atom-Atom	Bond length (Å)	Atom-Atom	Bond length (Å)	Atom-Atom	Bond length (Å)
C1-S1	1.780(4)	S2-C31	1.779(4)	C1-C2	1.381(6)
C19-C20	1.375(6)	C1-C6	1.382(7)	C19-C24	1.382(6)
S1-C7	1.792(4)	S1-C13	1.788(4)	C20-C21	1.382(6)
C2-C3	1.394(7)	C21-C22	1.387(8)	C3-C4	1.357(9)
C22-C23	1.373(8)	C4-C5	1.375(9)	C23-C24	1.380(6)
C5-C6	1.380(7)	C25-C26	1.373(6)	C25-C30	1.379(6)
C7-C8	1.378(6)	C7-C12	1.386(6)	C26-C27	1.384(8)
C8-C9	1.392(7)	C27-C28	1.367(8)	C9-C10	1.366(8)
C28-C29	1.381(8)	C10-C11	1.375(7)	C29-C30	1.375(7)
C11-C12	1.384(7)	C31-C32	1.371(7)	C31-C36	1.381(6)
C13-C14	1.394(6)	C13-C18	1.381(6)	C32-C33	1.384(8)
C14-C15	1.394(7)	C33-C34	1.367(9)	C15-C16	1.367(8)
C34-C35	1.372(9)	C16-C17	1.390(7)	C35-C36	1.378(7)
C17-C18	1.379(7)	Cl1-Cu1	2.2451(12)	Cu1-Cl2	2.2723(11)
S2-C19	1.786(4)	Cu1-Cl3	2.2364(13)	S2-C25	1.789(4)
Cu1-Cl4	2.2571(12)				

**Figure 1.** The molecular structure and atom labeling scheme of [TPS]₂[CuCl₄] with displacement ellipsoids drawn at the 50% probability level.**Figure 2.** A view along the *a*-axis direction of the crystal packing of [TPS]₂[CuCl₄].

The τ_4 value of 0.59 is comparable to those reported for related distorted tetrachlorocuprate(II) salts, appropriately described as seesaw geometry [16]. For example, 4-*tert*-butylpyridinium tetrachlorocuprate(II) contains two crystallographically independent [CuCl₄]²⁻ anions with Cu-Cl distances of 2.2391(12)-2.2790(12) Å, Cl-Cu-Cl angles of 96.46(5)-140.37(6)° and 94.75(5)-137.91(6)°, and τ_4 values of 0.58 and 0.55 [17]. Similarly, bis(2-methylpyridinium)

tetrachlorocuprate(II) shows Cl-Cu-Cl angles of 98.55(2)-137.4(3)° and Cu-Cl distances of 2.249(1)-2.250(1) Å, with an τ_4 value of 0.67 [18], while bis(2-amino-6-bromopyridinium) tetrachlorocuprate(II) has Cu-Cl distances of 2.211(3)-2.287(3) Å, Cl-Cu-Cl angles of 98.0(1)-131.0(1)°, and τ_4 = 0.69 [19]. Therefore, the [CuCl₄]²⁻ anion in the title compound falls within the range observed for flattened and distorted tetrahedral tetrachlorocuprate (II) anions.

Table 3. Bond angles of the [TPS]₂[CuCl₄] complex.

Atom-Atom-Atom	Bond angle (°)	Atom-Atom-Atom	Bond angle (°)	Atom-Atom-Atom	Bond angle (°)
C2-C1-S1	115.1(3)	C20-C19-S2	114.1(3)	C6-C1-S1	122.8(4)
C24-C19-S2	122.3(3)	C1-S1-C7	103.6(2)	C1-S1-C13	104.97(19)
C13-S1-C7	104.89(19)	C26-C25-S2	123.6(3)	C30-C25-S2	114.7(3)
C8-C7-S1	122.0(4)	C12-C7-S1	116.4(3)	C32-C31-S2	115.3(3)
C36-C31-S2	122.5(4)	C14-C13-S1	114.7(3)	C18-C13-S1	122.8(3)
Cl1-Cu1-Cl2	98.43(5)	Cl1-Cu1-Cl4	96.15(5)	Cl3-Cu1-Cl1	136.98(6)
C19-S2-C25	103.66(19)	Cl3-Cu1-Cl2	96.45(5)	C31-S2-C19	105.40(19)
Cl3-Cu1-Cl4	98.00(6)	C31-S2-C25	103.97(19)	Cl4-Cu1-Cl2	139.70(5)

Previously reported TPS⁺ salts show S-C bond lengths generally in the 1.77–1.80 Å range and C-S-C angles of about 100–107° [11–13]. Related tetrachlorometallate analogues show M-Cl distances of 2.19–2.38 Å and Cl-M-Cl angles of approximately 104–113° [13]. Overall, the bond distances and angles are consistent with related TPS⁺ cation and tetrachlorometallate systems that we have previously reported [11–13]. Bond distances and angles are listed in Tables 2 and 3, respectively.

Figure 2 shows the unit cell and packing in the complex viewed along the *a*-axis. There is no π - π stacking observed in the structure or other significant intermolecular interactions. Close contacts within the sums of the van der Waals radii are depicted with S1-Cu1 and S2-Cu1 distance of 3.6527(12) Å and 3.6927(12) Å, respectively.

4. Conclusions

The complex salt, composed of two triphenylsulfonium cations and one tetrachlorocuprate(II) anion, was synthesized in a modest yield from a 2:1 reaction of triphenylsulfonium chloride and copper(II) chloride dihydrate. The crystals were grown by slow evaporation of solvent, and the structure was solved by single-crystal X-ray crystallography at ambient temperature. The structure presents two independent triphenylsulfonium cations and a distorted four-coordinate tetrachlorocuprate(II) anion.

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Supporting information

CCDC-2519435 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered to. Sample availability: Samples of the compound are available from the author.

CRediT authorship contribution statement

Conceptualization: Will Lynch, Clifford Padgett; Methodology: Will Lynch, Clifford Padgett; Validation: Will Lynch, Clifford Padgett; Formal Analysis: Will Lynch, Clifford Padgett; Investigation: Grace Bennett, Kennedy Gaines, Morgan Barry, Mark Gillican, Clifford Padgett, Will Lynch; Resources: Grace Bennett, Kennedy Gaines, Morgan Barry, Mark Gillican, Clifford Padgett, Will Lynch; Data Curation: Grace Bennett, Kennedy Gaines, Morgan Barry, Mark Gillican, Clifford Padgett, Will Lynch; Writing - Original Draft: Grace Bennett, Kennedy Gaines, Morgan Barry, Mark Gillican, Clifford Padgett, Will Lynch; Writing - Review and Editing: Will Lynch, Clifford Padgett; Visualization: Clifford Padgett, Will Lynch; Funding acquisition: Will Lynch; Supervision: Will Lynch; Project Administration: Will Lynch.

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ORCID and Email

Grace Bennett

 gs09195@georgiasouthern.edu

 <https://orcid.org/0009-0004-6111-5351>

Kennedy Gaines

 kg17381@georgiasouthern.edu

 <https://orcid.org/0009-0008-1413-9536>

Morgan Barry

 lb20717@georgiasouthern.edu

 <https://orcid.org/0009-0009-0698-0832>

Mark Gillican

 mg14243@georgiasouthern.edu

 <https://orcid.org/0009-0004-4398-5070>

Clifford Padgett

 cpadgett@georgiasouthern.edu

 <https://orcid.org/0000-0002-8373-1495>

Will Lynch

 wlynch@georgiasouthern.edu

 <https://orcid.org/0000-0003-3494-8652>

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