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Synthesis and Characterization of Semiconductive Dichloridobis(thianthrene)gold(1+) Tetrachloridoaurate(1–)

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A new (thianthrene)gold(III) complex has been synthesized in liquid SO_2 as the solvent from thianthrene (TA) and $AuCl_3$. $[AuCl_2(TA)_2][AuCl_4]$ [triclinic, $P\bar{1}$, $a = 9.9832(2)$ Å, $b = 10.3404(2)$ Å, $c = 15.0798(4)$ Å, $\alpha = 75.038(1)°$, $\beta = 81.610(1)°$, $\gamma = 68.409(1)°$, $V = 1396.15(5)$ Å^3, $Z = 2$] has a salt-like structure consisting of $[AuCl_2(TA)_2]^+$ and $[AuCl_4]^-$ ions, both with square-planar coordinated gold atoms of oxidation state +3. In the cation, two bent TA molecules are coordinated to Au each through one sulfur atom. The title compound is thermally stable up to 425 K and is semiconducting with a conductivity reaching 25 $mS m^{-1}$ at 380 K and a low activation energy of 0.43 eV. A model for the charge transport along the stacked cationic complexes is discussed. When dissolved in chloroform $[AuCl_2(TA)_2][AuCl_4]$ is converted into the already known uncharged, mononuclear complex $[AuCl_3(TA)]$, which shows that a polymerization isomerism exists between the two forms.

Introduction

Thianthrene (TA) (Figure 1, left) is a heterocyclic molecule bearing two sulfur atoms. It was expected that TA could serve as a mono- as well as a bidentate ligand towards metal ions.[1] The molecule is bent along the S···S axis by 128° at room temperature in the crystalline state as shown by structure determination.[2] The two sulfur atoms have thus in principle the possibility to bond simultaneously to one metal centre. The results from early attempts to prepare complexes of thianthrene with nickel,[3] palladium, platinum,[4] ruthenium,[5] silver, rhodium, iridium and gold,[6] the last mentioned with crystallographic support,[7] indicate that TA behaves preferably as a monodentate ligand. By means of Job's method of continuous variation and microanalysis, the metal/ligand ratios in the Pt^{II} or Pd^{II} complexes are known to vary with the solvent used.[4] Whereas these two metals form complexes up to a 1:2 metal/ligand ratio, iridium is claimed to form complexes with a 1:3 metal/ligand ratio.[6]

The reaction of $AuCl_3$ and TA in $CHCl_3$ is known to give a 1:1 complex, $[AuCl_3(TA)]$, with only one of the sulfur atoms attached to the square-planar coordinated Au atom (Figure 1, right).[7] This structure confirmed the previously reported NMR investigation of TA complexes of silver indicating that TA coordinates the metal ion through one sulfur atom.[8] Apart from this earlier work there is only one structure known with TA acting as a bidentate and chelating ligand. The structure of $[Ag(ClO_4)(TA)]_2$ consists of dimeric complexes with Ag^+ ions coordinated by two sulfur atoms of one TA molecule,[9] one oxygen atom of a perchlorate ion and two carbon atoms of a phenyl ring of the second TA molecule. An expanded system is formed from $AgClO_4$ and a macrocyclic thianthrenophane.[10] Here, Ag^+ ions are coordinated by four S atoms of two thianthrenophane molecules leading to a chain-like polymer.

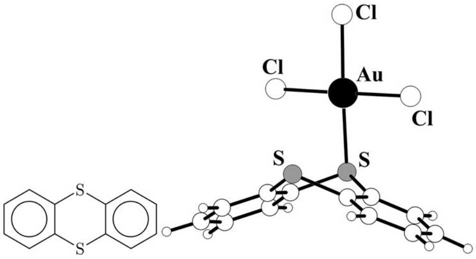

Figure 1. Formula of thianthrene (left) and the molecular structure of the respective gold(III) complex $[AuCl_3(TA)]$[7] (right).

Recently performed syntheses of TA complexes in liquid SO_2[11] underlined that the complexation reaction of thianthrene with silver ions is influenced by the solvent. In the crystal structures of $[Ag_2(TA)_2][BF_4]_2{\cdot}3SO_2$ and $[Ag_2(TA)_3][SbF_6]{\cdot}5SO_2$ both sulfur atoms of thianthrene are coordinated to two silver ions. Furthermore, there is more than one thianthrene molecule simultaneously bound to two metal centres. The use of liquid SO_2 and the weakly coordinating anions increased the number of coordinating bonds from one metal ion to the sulfur atom of thianthrene.

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Inspired by the previous results of (thianthrene)silver complexes, we performed the synthesis of a new (thianthrene)gold complex in liquid SO_2 and demonstrate again the strong influence of the solvent used for the nature of the complex formed.

Results and Discussion

Crystal Structure

Black crystals of dichloridobis(thianthrene)gold(1+) tetrachloridoaurate(1–), $[AuCl_2(TA)_2][AuCl_4]$ precipitated from the reaction of $AuCl_3$ and TA in liquid SO_2 as the only product. The crystal-structure determination shows the structure to consist of $[AuCl_2(TA)_2]^+$ and $[AuCl_4]^-$ ions. The asymmetric unit contains two independent cations and anions, both located with their gold atoms at special positions on inversion centres giving all cations and anions crystallographic C_i symmetry (Figure 2).

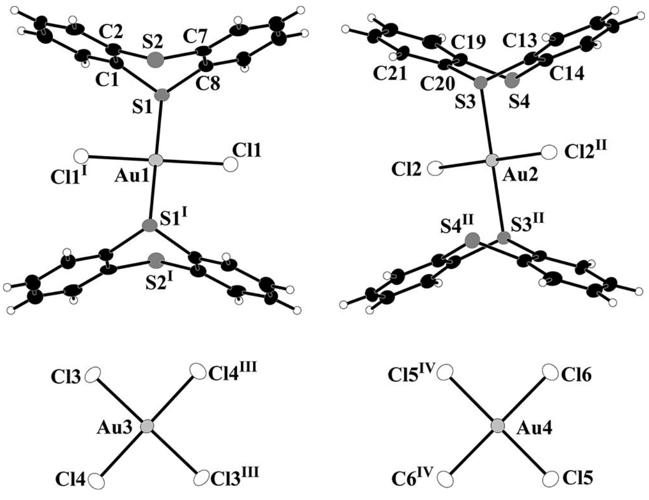

Figure 2. Two independent $[AuCl_2(TA)_2]^+$ cations and two independent $[AuCl_4]^-$ anions in the structure of $[AuCl_2(TA)_2][AuCl_4]$. Thermal ellipsoids are scaled to include a probability density of 50%. Hydrogen atoms are drawn as spheres with arbitrary radii. Symmetry operations: I: $1 - x$, $2 - y$, $2 - z$; II: $2 - x$, $1 - y$, $1 - z$; III: $1 - x$, $1 - y$, $2 - z$; IV: $1 - x$, $1 - y$, $1 - z$.

In the cation two thianthrene molecules are coordinated to the gold atom each through one sulfur atom in *trans* position of the square-planar coordination environment, typical for Au^{III}. The two independent complexes show small but significant differences in the structural parameters: whereas both Au–Cl bonds have identical lengths of 2.28 Å, Au–S1 amounts to 2.41 and Au2–S3 to 2.40 Å. The Cl–Au–S angles amount to 88.0 and 92.0° in cation 1 and 85.5 and 94.5° in cation 2. The S···S–Au angle in cation 1 is 74.4° but amounts to 81.5° in cation 2. The torsion along S···S–Au–Cl is significantly larger in cation 1 with 85.6° than in cation 2 with 67.7°. The shape of the coordinated TA molecules is not substantially altered in comparison to the uncoordinated state. The interplanar angle of the folded TA ligands amounts to 131.32° in cation 1 and 133.74° in cation 2. These values as well as the bond lengths in the molecules are equivalent to neat thianthrene (Tables 1 and 2).

Table 1. Selected bond lengths in the structure of $[AuCl_2(TA)_2]$-$[AuCl_4]$.

Bond	Length [Å]	Bond	Length [Å]
Au1–Cl1	2.277(2)	S1–C8	1.767(7)
Au1–S1	2.412(2)	S1–C1	1.768(7)
Au2–Cl2	2.280(2)	S2–C2	1.760(8)
Au2–S3	2.400(2)	S2–C7	1.769(8)
Au3–Cl3	2.275(2)	S3–C13	1.764(8)
Au3–Cl4	2.276(2)	S3–C20	1.780(7)
Au4–Cl6	2.280(2)	S4–C14	1.767(7)
Au4–Cl5	2.281(2)	S4–C19	1.771(7)

Table 2. Selected bond angles in the structure of $[AuCl_2(TA)_2]$-$[AuCl_4]$.

Bond	Angle [°]	Bond	Angle [°]
C13–S3–Au2	104.2(2)	Cl6–Au4–Cl5^{IV}	89.34(7)
C13–S3–C20	101.7(3)	Cl3–Au3–Cl3^{III}	180.0
C14–S4–C19	101.0(3)	Cl2–Au2–Cl2^{II}	180.0
C1–S1–Au1	103.1(2)	S1–Au1–S1^{I}	180.0
C20–S3–Au2	107.3(2)	S3^{II}–Au2–S3	180.0
C2–S2–C7	101.6(3)	Cl5–Au4–Cl5^{IV}	180.0
C8–S1–Au1	103.5(2)	Cl2–Au2–S3^{II}	85.53(6)
C8–S1–C1	101.1(3)	Cl4–Au3–Cl4^{III}	180.0
Cl1–Au1–Cl1^{I}	180.0	Cl3^{IV}–Au3–Cl4	89.52(7)
Cl1–Au1–S1	87.99(6)	Cl6^{IV}–Au4–Cl6	180.0

The two independent anions are almost isostructural. The Au atoms are coordinated by four Cl atoms in an undistorted square-planar fashion. Despite the crystallographic symmetry being only C_i, the ideal symmetry D_{4h} is nearly fulfilled. The Au–Cl bonds amount on average to 2.28 Å, and the Cl–Au–Cl angles deviate less than 1° from rectangularity.

In the unit cell the cationic complexes face each other via the thianthrene ligands resulting in chains of cations running along the –111 direction (Figure 3). The S···S axes of neighbouring TA ligands are in an almost orthogonal orientation to each other, and one of the benzene rings of

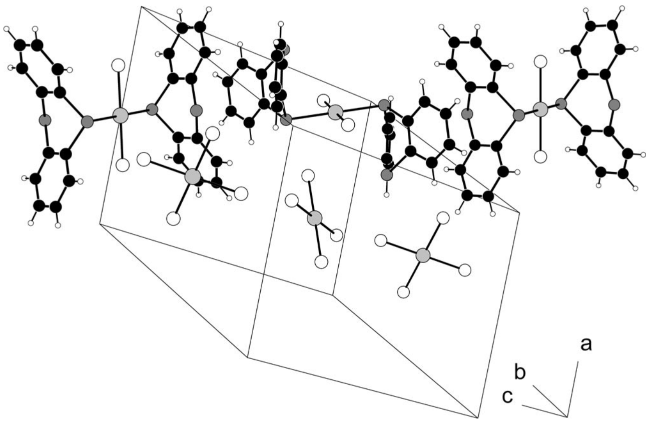

Figure 3. Arrangement of the ions in the unit cell of $[AuCl_2(TA)_2]$-$[AuCl_4]$ showing the stacked arrangement of the $[AuCl_2(TA)_2]^+$ cations. All atoms are drawn as spheres with arbitrary radii.

each complex is located in the bowl-shaped void formed by the TA ligand of the neighbouring complex. The shortest intermolecular C···C distance, found between C21 and C7, amounts to 3.42 Å. These chains are surrounded by the $[AuCl_4]^-$ anions and are therefore isolated from each other.

Vibrational Spectroscopy

The IR spectrum of the complex salt differs considerably from that of free thianthrene showing some additional bands and a shift of bands. The IR vibrational spectrum of thianthrene has been thoroughly studied.[13,14] The obvious differences in the spectra appear predominantly for C–S vibrations but are also present for C–C and C–H modes. For example, the stretching out-of-plane deformation modes, observed for thianthrene at 476, 1086 and 1101 cm^{-1} are observed for $[AuCl_2(TA)_2][AuCl_4]$ at 470, 1077 and 1116 cm^{-1}. Several other absorption bands, attributed to C–H deformation and C–C stretching modes are also shifted by up to 10 cm^{-1} to higher and lower energies. Because of the black colour of the compound we did not succeed in recording a Raman spectrum. Even at low laser power only strong fluorescence was observed.

Thermal Properties

$[AuCl_2(TA)_2][AuCl_4]$ is thermally stable up to 438 K. At this temperature the decomposition was detected visually. In the DSC (differential scanning calorimetry) measurements a very small endothermic effect around 350 K appeared, which, however, was only detected during the first heating and did not appear again in the subsequent heating/cooling cycles (Figure 4). The title compound can be heated up to 425 K without decomposition or alteration, and no signs of solid-state phase transitions were detected.

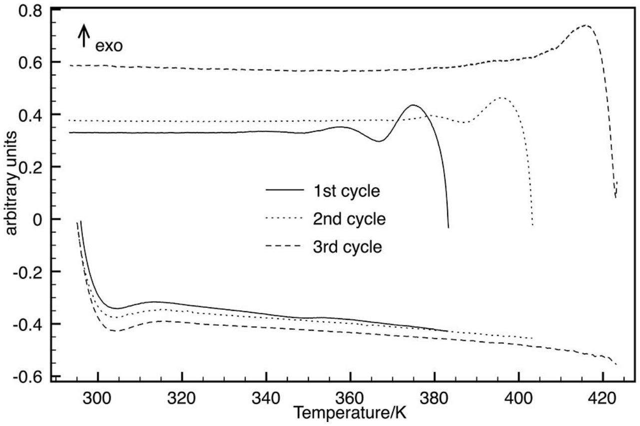

Figure 4. DSC measurement of $[AuCl_2(TA)_2][AuCl_4]$. Three cycles of heating/cooling were performed. Each cycle starts from room temperature to an upper set point and back to ambient temperature at a rate of 10 $K\,min^{-1}$ for both directions. The highest applied temperatures were 383 K, 403 K and 423 K at the top of the 1st, 2nd and 3rd cycle, respectively.

Electrical Conductivity

At room temperature the electrical conductivity of $[AuCl_2(TA)_2][AuCl_4]$, determined by the two-probe technique, is very low. Since the DSC measurement showed enhanced thermal stability, the conductivity measurements were expanded up to 390 K. Up to this temperature thermal decomposition can be excluded. The specific conductivity reaches 25 mSm^{-1} with semiconducting thermal behaviour (Figure 5). The activation energy for the conductivity process can be obtained by applying the Arrhenius law. The function $\ln(\sigma) = f(T^{-1})$ allows for a linear fit with good correlation between data and the regression line. The activation energy is 0.43 eV.

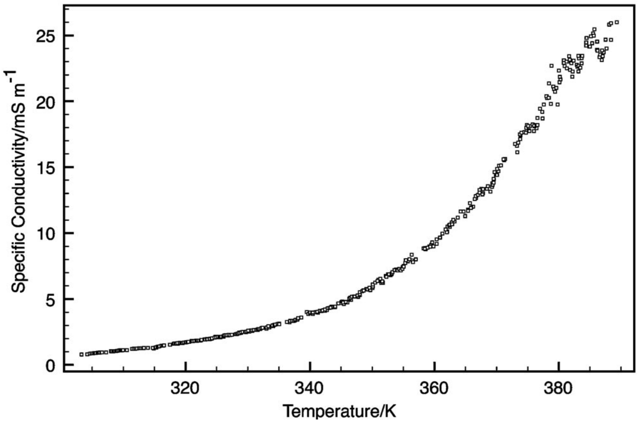

Figure 5. Specific conductivity of $[AuCl_2(TA)_2][AuCl_4]$ in the temperature range between room temperature and 390 K, determined by a two-probe measurement. Applied voltage 1 V.

The low activation energy and the relatively high conductivity of $[AuCl_2(TA)_2][AuCl_4]$ is surprising, since at first glance the salt-like character does not imply such behaviour. The black colour of the compound, however, is in line with the low thermal barrier (Figure 6).

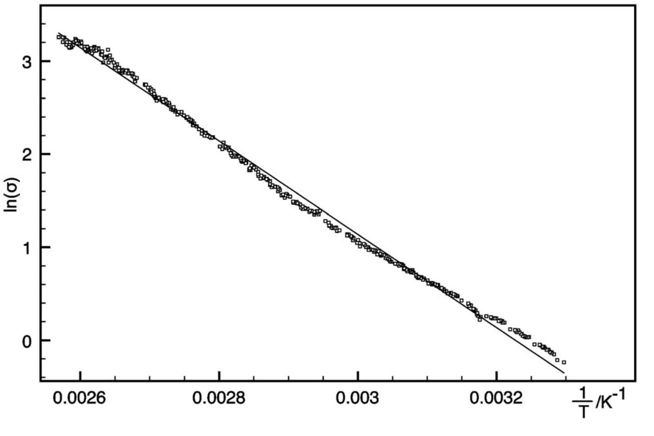

Figure 6. Arrhenius plot for the determination of the thermal activation energy E of $[AuCl_2(TA)_2][AuCl_4]$ according to $\ln\sigma = -E/kT + \ln\sigma_0$. The regression line shows a satisfying linear fit. The Boltzmann constant is 8.617343×10^{-5} $eV\,K^{-1}$.

The conductivity can be explained by an electron-transport model along the chains of the cations (Figure 3). Assigning normal valences with Au^{III} and neutral thianthrene ligands, these chains can be formulated as $\cdots TA^0$–

$Au^{III}Cl_2^+$–TA^0···TA^0–$Au^{III}Cl_2^+$–TA^0··· with one positive charge per (TA^0–$Au^{III}Cl_2$–TA^0)$^+$ unit. A local electron transfer from neutral TA, which is known to be easily oxidized to the respective radical cation,[15] to Au^{III}, which is known to be a strong oxidizing agent, leads to ···TA^+–$Au^ICl_2^-$–TA^+···TA–$Au^{III}Cl_2^+$–TA···. This charge transfer retains the overall charge of the individual cationic complexes. Electron exchange between neighbouring oxidized and neutral thianthrene molecules would allow for transferring charge along the chains. This model, however, implies a through-space electron transfer. Since the thianthrene ligands of neighbouring complexes are separated from each other by the van der Waals radius, generally higher activation energies are expected than actually found. Thermal activation is implicitly necessary for the electron transfer, and substantial conductivity is only achieved well above ambient temperature.

Reflectance Spectrum

Diffuse reflectance spectra of $[AuCl_2(TA)_2][AuCl_4]$ have been measured with samples diluted with $BaSO_4$. Evaluated with the Kubelka–Munk function, the reflectance increases gradually up to the highest wavelength measured, 800 nm, with a steeper increment above 650 nm. There is no discernible peak or edge observable in the visible region between 470 and 800 nm. This is in line with the low observed activation energy, which would correspond to a spectral edge below 2500 nm in the infrared region.

Dissolution Properties and Isomerism

The reaction of thianthrene and $AuCl_3$ in $CHCl_3$ is known to yield the mononuclear, uncharged complex $[AuCl_3(TA)]$.[7] Since $[AuCl_2(TA)_2][AuCl_4]$ has the equivalent formula but doubled molecular weight, it was desirable to examine the behaviour of $[AuCl_2(TA)_2][AuCl_4]$ when dissolved in chloroform, which is a much less polar solvent than liquid SO_2. On mixing $[AuCl_2(TA)_2][AuCl_4]$ with $CHCl_3$ some decomposition occurs, observable by the precipitation of finely dispersed metallic gold. The black crystals of $[AuCl_2(TA)_2][AuCl_4]$ show only a limited solubility in $CHCl_3$, but after one week the majority of them were converted into dark red, transparent, needle-shaped crystals. The determination of the lattice constants on selected single crystals (a = 12.99, b = 14.37, c = 5.40 Å, β = 103.1°, V = 983.4 Å^3 at 296 K) showed that $[AuCl_2(TA)_2][AuCl_4]$ underwent transformation to $[AuCl_3(TA)]$ (a = 12.88, b = 14.27, c = 5.33 Å, β = 103.2°, V = 955.4 Å^3 at 203 K[7]).

The complex formation between thianthrene and $AuCl_3$ is therefore strongly solvent-dependent. The polar solvent SO_2 supports the Lewis acid/base ionization of $AuCl_3$ into $[AuCl_2]^+$ and $[AuCl_4]^-$. $[AuCl_2]^+$ is then coordinatively saturated by two TA molecules to give $[AuCl_2(TA)_2][AuCl_4]$. The less polar solvent $CHCl_3$ supports the formation of neutral complexes and leads to the monomer $[AuCl_3(TA)]$. There is an equilibrium between the two forms according to the equation:

$$2\,[AuCl_3(TA)] \rightleftharpoons [AuCl_2(TA)_2][AuCl_4]$$

Isomerism of this type has long been known and is termed "polymerization isomerism". A classical textbook example is the two forms of $PtCl_2·2NH_3$, namely $[PtCl_2(NH_3)_2]$ (*cis*-Platin or Peyrone's salt) and $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt).

Conclusions

The reaction of thianthrene with $AuCl_3$ yields either the uncharged, mononuclear, dark red complex $[AuCl_3(TA)]$ or the ionic, black, salt-like form $[AuCl_2(TA)_2][AuCl_4]$, depending on the solvent used. The uncharged, molecular form is obtained in less polar solvents like $CHCl_3$, the ionic form in the polar solvent liquid SO_2. In both forms thianthrene acts as a monodentate ligand towards the three-valent gold atom. Dissolution of the ionic form in $CHCl_3$ yields the uncharged form indicating a reversible equilibrium. As a remarkable feature, the ionic form shows an electrical conductivity of 25 mSm^{-1} with semiconducting behaviour and low activation energy of 0.43 eV.

Experimental Section

General: Liquid SO_2 was purchased from Air Products and stored over P_4O_{10} before use. Thianthrene was purchased from Aldrich and recrystallized from ethanol/toluene. Gold(III) chloride was prepared from gold metal and dry chlorine and sublimed in a glass ampoule before use. The sample of $[AuCl_2(TA)_2][AuCl_4]$ for IR spectroscopy was pressed to a KBr disc and measured with a Bruker IFS 113v FTIR spectrometer. X-ray diffraction data were collected with a Bruker-Nonius Kappa-CCD diffractometer equipped with an Oxford Cryostream cooling device. DSC measurements were performed with a Netzsch DSC 204 F1 Phoenix instrument. Determination of the gold content was carried out by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with an IRIS Advantage instrument, Thermo Jarrel Ash Corporation. The analysis of the chlorine content was performed by potentiometric titration with $AgNO_3$ using a Metrohm Titrino instrument. UV/Vis measurements were performed with a Gröbel UV-Elektronik spectrometer.

Dichloridobis(thianthrene)gold(1+) Tetrachloridoaurate(1–): Thianthrene (142.3 mg, 0.658 mmol) and gold(III) chloride (199 mg, 0.656 mmol) were weighed under dry argon into separate branches of an H-shaped reaction vessel equipped with Teflon screw cocks (Young Ltd., London).[16] Liquid SO_2 (20 mL) was condensed into both sides leaving the largest part of $AuCl_3$ undissolved. Thianthrene dissolved completely forming a bright yellow solution. This solution was then poured into the other branch so that finally all liquids were collected in the branch where the $AuCl_3$ was placed. The tube was shaken thoroughly in 15 min intervals, and the colour of the solution mixture turned red within several hours. Small black crystals were already observable after 1 d. After two months, all of the $AuCl_3$ was converted to black crystals of $[AuCl_2(TA)_2][AuCl_4]$. $C_{24}H_{16}Au_2Cl_6S_4$ (1039.304): calcd. C 27.74, H 1.55, Au 37.90, Cl

20.47, S 12.34; found C 27.33, H 1.78, Au 37.55, Cl 20.2, S 12.79. The melting point was 438 K, measured visually.

X-ray Structure Determination: A black single crystal was selected from the red solution under inert conditions. Diffraction data collection was performed at 110 K. When covered by a thin layer of inert oil, the crystals are actually stable in open air for weeks. All calculations were performed by using the SHELX-97 crystallography program suite.[17] The absorption correction method used was *multiscan*.[18] The hydrogen atoms were added at calculated positions and refined riding on their C atoms with the isotropic displacement parameter fixed to $1.2B_H = B_C$. Details of the crystal data collection, structure analysis and refinement are given in Table 3. Selected bond lengths and angles are listed in Tables 1 and 2. CCDC-701198 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.

Table 3. Refinement data.

Empirical formula	$C_{24}H_{16}Au_2Cl_6S_4$
a [Å]	9.9832(2)
b [Å]	10.3404(2)
c [Å]	15.0798(4)
α [°]	75.038(1)
β [°]	81.610(1)
γ [°]	68.409(1)
V [Å^3]	1396.15(5)
Z	2
$\rho_{\text{calcd.}}$ [g cm^{-3}]	2.472
μ [mm]$^{-1}$	11.386
Crystal system, space group	triclinic, $P\bar{1}$ (no. 2)
Diffractometer	Bruker-Nonius Kappa-CCD
λ(Mo-K_α) [Å]	0.71073
T [K]	110
θ range [°]	3.14–27.55
hkl range	$-12 \le h \le 12$ $-13 \le k \le 13$ $-19 \le l \le 19$
No. of data collected	51960
No. of independent reflections, R_{merge}	6392, 0.091
No. of refined parameters	331
Ratio reflections/parameters	19.31
R values	$wR(F^2) = 0.090$ $R(\lvert F\rvert) = 0.0516$ (all 6392 reflections) $R(\lvert F\rvert) = 0.0365$ (5195 reflections) with $F_o > 4\sigma(F_o)$
GoF	1.181
Largest difference peak/hole [e Å^{-3}]	+1.750/–2.267

Conductivity Measurement: Conductivity measurements were performed under dry and inert conditions with a conventional two-electrode technique. The sample was placed in a 30 mm long quartz tube with an outer and inner diameter of 4.05 and 2.0 mm, respectively, and was pressed manually from opposite directions between the electrodes, which were made of stainless steel. Both electrodes were held by two metal springs to keep the sample under constant static pressure in the middle of the quartz tube. The disc-shaped sample had a thickness of 0.7 mm. Variation of temperature was achieved with a cylindrical micro-oven equipped with a thermocouple as the temperature sensor. The length and outer diameter of the micro-oven were 24 mm and 15 mm, respectively. The central hole of the oven, in which the quartz tube with the sample was inserted had an inner diameter of 4.10 mm. The temperature change rate during the measurement was 30 K h^{-1} up- and downward, programmed between 303 and 390 K.

Acknowledgments

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