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Note

The synthesis of triethylphosphine gold(I) 4-nitrobenzenethiolate and solvent dependent visible absorption spectra of 4-nitrobenzenethiolate

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ABSTRACT

The synthesis of triethylphosphine gold(I) 4-nitrobenzenethiolate, $Et_3PAu(SC_6H_4NO_2\text{-}4)$, is reported. $Et_3PAu(SC_6H_4NO_2\text{-}4)$ displays a low energy visible electronic absorption band which is solvent dependent: EtOH ($\lambda_{max} = 385$ nm), acetonitrile ($\lambda_{max} = 391$ nm), THF ($\lambda_{max} = 395$ nm), and DMSO ($\lambda_{max} = 402$ nm). The corresponding low energy visible electronic absorption band of 4-nitrobenzenethiolate, $4\text{-}NO_2C_6H_4S^-$ also shows solvent dependency: acetonitrile, ($\lambda_{max} = 484$ nm), DMSO ($\lambda_{max} = 502$ nm), dimethylformamide ($\lambda_{max} = 505$ nm). The positive solvatochromic shifts for $Et_3PAu(SC_6H_4NO_2\text{-}4)$ and $4\text{-}NO_2C_6H_4S^-$ are consistent with an intraligand (IL) charge transfer transition, i.e. $\pi(S) \rightarrow {}^*\pi$ ($C_6H_4NO_2$-4) or $n(S) \rightarrow {}^*\pi$ ($C_6H_4NO_2$-4). Assignment of $4\text{-}NO_2C_6H_4S^-$ was aided by a DFT calculation.

1. Introduction

The reactivity of gold(I) thiolate complexes includes exchange with disulfide, sulfur based oxidation at low oxidation potentials, e.g. ⩽0.6 V vs. SCE, gold based oxidation at higher potentials [1–13], as well as the recent example of oxidative addition of a fluorinated disulfide to an anionic bisthiolate gold(I) complex [14]. It has been shown that the reaction of a symmetrical disulfide (*RSSR*) with phosphine gold(I) thiolate (PR_3AuSR) complexes often proceeds with initial production of asymmetric disulfide (*RSSR). For example, in the reaction of bis(diphenylphosphino)methane $Au_2(SC_6H_4CH_3\text{-}4)_2$ and $(4\text{-}ClC_6H_4S)_2$ the asymmetric disulfide, $ClC_6H_4SSC_6H_4CH_3$, forms first [12]. A preliminary study on the solvent dependent kinetics of the exchange of the disulfide, $(SC_6H_4NO_2\text{-}4)_2$, with auranofin (2,3,4,6-tetraacetyl-1-thio-D-glucopyranosato(triethylphosphine) gold(I)) has recently been reported [1]. The product, $Et_3PAu(SC_6H_4NO_2\text{-}4)$, is purported to form based in part on the appearance of a visible absorption band at about 400 nm, which was assigned by analogy to $Ph_3PAu(SC_6H_4NO_2\text{-}4)$ [15] and $Cy_3PAu(SC_6H_4NO_2\text{-}4)$ [16]. The kinetics of this reaction are complicated owing to a solvent dependency on rate of reaction [1], a secondary reaction involving the asymmetric disulfide and auranofin, and the possible formation of a gold coordinated disulfide precursor complex (in analogy with zinc-thiolate disulfide exchange) [17]. In order to understand the reaction in more detail, we have synthesized $Et_3PAu(SC_6H_4NO_2\text{-}4)$ and studied the visible absorption spectra of this gold(I) complex, as well as the corresponding 4-nitrobenzenethiolate ($4\text{-}NO_2C_6H_4S^-$), as a function of solvent.

2. Experimental

2.1. Chemicals and Instruments

Anhydrous acetonitrile (ACN, Baker), anhydrous tetrahydrofuran (THF, Baker or 99+%, Sigma), anhydrous dimethyl sulfoxide (DMSO, Burdick & Jackson or 99.9%, Sigma), absolute ethanol (Pharmco-Aaper), dimethylformamide (DMF, 99%, Sigma), hexanes (Baker), methanol (Fisher), methylene chloride (CH_2Cl_2, Fisher), pyridine (anhydrous 99.8%, Sigma), sodium methoxide (Sigma), toluene (Fisher), and triethylphosphine gold(I)chloride (Sigma) were used as received. Technical grade 4-nitrobenzenethiol (80%, Sigma) was purified by dissolving it in degassed ethanol followed by filtration of insoluble material. The thiol was recovered by removing the solvent under vacuum. Tetra-*n*-butylammonium tetrafluoroborate 99% (Bu_4NBF_4, Sigma) was recrystallized 3× from methylene chloride and ether (Fisher). The anhydrous solvents were septum sealed, packaged under nitrogen or argon, and stored in a DriLab Model HE-493 glove box. Instrumentation included an EG&G Potentiostat/Galvanostat Model 273, Beckman DU 7400 Diode Array UV–Vis Spectrophotometer, and XL-300 MHz Varian NMR. The Gutman donor numbers were taken from Inorganic Electronic Spectroscopy by Lever, Table 5.2, pg. 211 [18].

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2.2. Synthesis of $Et_3PAu(SC_6H_4NO_2\text{-}4)$

4-Nitrobenzenethiol ($4\text{-}NO_2C_6H_4SH$, 38.8 mg, 0.25 mmol) was added to a solution of sodium methoxide (13.7 mg, 0.25 mmol) in methanol. A solution of triethylphosphinegold(I)chloride (88.6 mg, 0.25 mmol) in CH_2Cl_2 was added dropwise. The mixture was allowed to stir at room temperature (2 h) before the solvent was evaporated in vacuo. The solid was dissolved in CH_2Cl_2 and the solution filtered through diatomaceous earth. Precipitation in hexanes yielded a bright yellow solid. Purification was accomplished through three successive recrystallizations in 1:1 toluene:hexanes followed by washing with hexanes. Yield: 69.5 mg, 60%. *Anal.* Calc. for $C_{12}H_{19}PAuSNO_2$ (469.29): C, 30.71; H, 4.08. Found: C, 30.70; H, 3.93%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.92$ (d, $J = 9.0$ Hz, 2H, aryl H *ortho* to NO_2), 7.60 (d, $J = 9.0$ Hz, aryl H *meta* to NO_2), 1.90 (dq, $J_{PH} = 9.9$ Hz, $J_{HH} = 7.8$ Hz, 6H, ethyl CH_2), 1.25 (dt, $J_{PH} = 18.9$ Hz, $J_{HH} = 7.8$ Hz, 9H, ethyl CH_3).

2.3. Visible absorption spectra of $Et_3PAu(SC_6H_4NO_2\text{-}4)$

Solutions for visible spectral analysis were prepared by serial dilution in a glove box. The following illustrates the procedure: a 5.00 mL solution containing 5.6 mg (12 μmol) of $Et_3PAu(SC_6H_4NO_2\text{-}4)$ in anhydrous DMSO was prepared (2.4 mM); a 200 μL aliquot of this solution was diluted to 10.00 mL resulting in a 40.0 μM solution. Two quartz cuvettes were filled with sample and solvent, respectively, capped, and removed from the glove box. The UV–Vis spectrophotometer was blanked versus air and spectra for solutions of $Et_3PAu(SC_6H_4NO_2\text{-}4)$ and solvent were recorded, respectively at room temperature (23 ± 1 °C). The solvent was subtracted after importing the data into Excel. The procedure used for solutions prepared with absolute ethanol was the same, except that it was done in the air on the bench top.

2.4. Visible absorption spectra of $4\text{-}NO_2C_6H_4S^-$

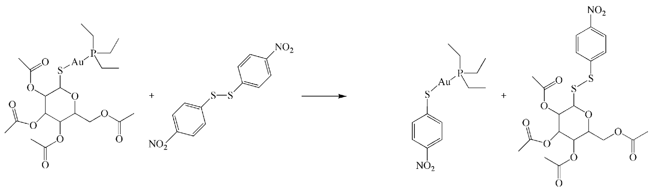
Solutions of technical grade $4\text{-}NO_2C_6H_4SH$ were used to generate 4-nitrobenzenethiolate, $4\text{-}NO_2C_6H_4S^-$. In acetonitrile and dimethylformamide, thiolate was generated by dropwise addition of a 0.1 M aqueous solution of KOH. In DMSO, DMAc and pyridine, solutions of $4\text{-}NO_2C_6H_4SH$ contained enough thiolate to record the spectrum without the addition of base. In DMSO, the thiolate peak was shown to decrease or increase by dropwise addition of aqueous 0.1 M HCl or 0.1 M KOH, respectively. In CH_2Cl_2 and THF, the salt, Bu_4NBF_4, was added to stabilize the thiolate. As a control experiment to test whether the presence of Bu_4NBF_4 shifts the peak position of the thiolate visible absorption band, $Bu_4NBF_4$was also added to DMSO solutions containing $4\text{-}NO_2C_6H_4S^-$. Addition of Bu_4NBF_4 does not shift the peak at 502 nm. Thiolate spectra were also generated electrochemically in 0.1 M Bu_4NBF_4 solutions of CH_2Cl_2 and THF, using a three-compartment electrochemical cell, separated by glass frits (SCE reference electrode: Pt working electrode: Pt auxiliary electrode). One to three milligrams of 4-nitrobenzenethiol was added to the working electrode compartment, which was very pale yellow prior to electrochemical reduction. A sufficiently negative voltage (e.g. −0.8 V vs. SCE) was then applied at the platinum working electrode while stirring to electrochemically generate the thiolate. Solutions of thiolate in CH_2Cl_2 and THF were transferred to a cuvette and recorded, respectively. Since thiolate solutions oxidize at approximately 0 V (vs. SCE) to disulfide [19], all solutions were expected to air oxidize to the disulfide. This was confirmed for all thiolate solutions: solutions were observed to bleach in color over time as a result of a decrease in the visible absorbance band assigned to thiolate.

2.5. DFT calculations of $4\text{-}NO_2C_6H_4S^-$

Calculations of the ground state of $4\text{-}NO_2C_6H_4S^-$ were completed in Gaussian 03 code using density functional theory (DFT) at the B3LYP level using the 6-31+G(p,d) basis set. The first singlet excited state of $4\text{-}NO_2C_6H_4S^-$ was calculated using the CI-Singles method using the same basis set. The dipole moment of the ground state was compared to the dipole moment of the singlet excited state, keeping the molecular orientation similar.

3. Results and discussion

Addition of auranofin [$(Et_3P)Au(TATG)$, TATG = 2,3,4,6-tetraacetyl-1-thio-D-glucopyranosato] to $(4\text{-}NO_2C_6H_4S)_2$ results in a decrease in the disulfide absorption band (ca. 320 nm) with a concomitant increase in absorption at ca. 400 nm [1]. The spectra evolve with an isosbestic point between the two absorption bands. As shown in equation 1, thiolate disulfide exchange would predict the formation of $Et_3PAu(SC_6H_4NO_2\text{-}4)$ and the asymmetric disulfide.



3.1. Syntheses and visible electronic spectra of $Et_3PAu(SC_6H_4NO_2\text{-}4)$

To help verify that the increase in absorption at ca. 400 nm is due to $Et_3PAu(SC_6H_4NO_2\text{-}4)$, as well as to determine the extinction coefficient to aid in kinetic analysis, $Et_3PAu(SC_6H_4NO_2\text{-}4)$ was independently synthesized by reaction of 4-nitrobenzenethiolate and chloro gold(I) triethylphosphine. Recrystallization from hexanes yields analytically pure, bright yellow needles. The visible spectra of $Et_3PAu(SC_6H_4NO_2\text{-}4)$ in various solvents match signals observed in the reaction of $(4\text{-}SC_6H_4NO_2)_2$ and auranofin (Eq. (1)). Fig. 1 shows the visible spectra of $Et_3PAu(SC_6H_4NO_2\text{-}4)$ in ACN, THF, and DMSO, with absorbance maxima at 390, 396, and 402 nm, respectively. The spectra are similar to the recently reported visible spectra of $Cy_3PAu(SC_6H_4NO_2\text{-}4)$ which has absorbance maxima at

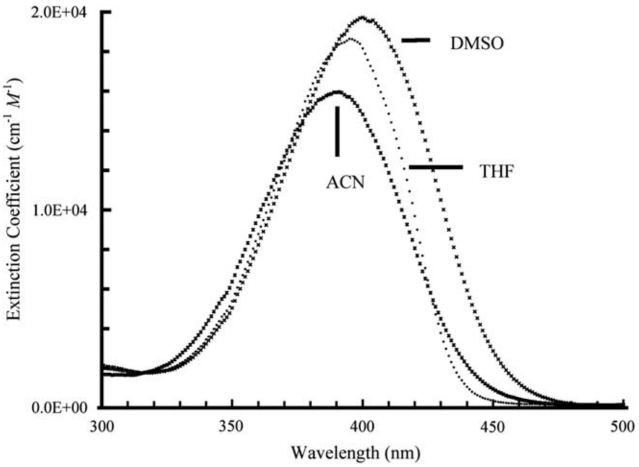


Fig. 1. Visible spectra of $Et_3PAu(SC_6H_4NO_2\text{-}4)$ in acetonitrile (ACN, $\lambda = 391$ nm), tetrahydrofuran (THF, $\lambda = 395$ nm), and dimethylsulfoxide (DMSO, $\lambda = 402$ nm).