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Synthesis and structure of gold(III) complexes of asymmetric dithiolene ligands

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We are pleased to mark Professor Malcolm Chisholm's many significant contributions to Inorganic Chemistry, using the occasion of his 60th birthday to congratulate him on his achievements, wishing him health, happiness, and continued scientific success.

Abstract

Four new [Au(dithiolene)₂]⁻ complexes, each involving two asymmetrically substituted dithiolene ligands (SC(H)C(R)S; R = phenyl, pyridin-2-yl, pyridin-3-yl, or pyridin-4-yl), have been synthesized by reacting K[AuCl₄] with the corresponding dithiolene, generated by base hydrolysis of the thione-protected 1,3-dithiolate. Each complex has been isolated as its [PPh₄]⁺ salt and the structures of these [PPh₄][Au(dithiolene)₂] compounds have been determined by X-ray crystallography; each anion possesses a square planar {AuS₄} core with a *cis*-arrangement of the R groups for R = phenyl and pyridin-2-yl complexes, but a *trans*-arrangement for R = pyridin-3-yl and pyridin-4-yl. In each compound, the lengths of the C–C (1.34 ± 0.01 Å) and C–S (1.75 0.03 Å) bonds of the metallocycle are consistent with the ene-1,2-dithiolate form of the dithiolene, i.e., these are [Au(III)bis(ene-1,2-dithiolate)]⁻ complexes. Each compound is diamagnetic and ¹H NMR studies indicate that, in solution in d⁶-acetone, both the *cis* and *trans* isomers of the [Au(SC(H)C(R)S)₂]⁻ anion are present and do not interconvert at room temperature. Each [Au(dithiolene)₂]⁻ complex an oxidation (80 < E_p^a < 230 mV) and a reduction (-1880 < E_p^c (red) < -2020 mV; versus [Fc]⁺/[Fc]); the particular potentials observed correlate with the electron withdrawing ability of the dithiolene substituent (R), as expressed by the Hammett σ_p -parameter. Comparison of the information obtained in these studies with that determined for related systems leads to the conclusion that the oxidation is a ligand-based process and that reduction involves addition of an electron to an orbital that possesses both metal and ligand character.

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Keywords: Gold; Dithiolene; Structure; Redox properties

1. Introduction

An extensive range of bis-dithiolene complexes of Au and their properties have been reported [1–31]; the majority are [Au(dithiolene)₂]⁻ complexes with a square planar {AuS₄} core, diamagnetic, and generally considered to involve a Au(III) (d⁸) centre. The redox properties of [Au(dithiolene)₂]⁻ complexes have been investigated and related $[Au(dithiolene)_2]^z$ (z = 0 or 2–) complexes identified [2-4,7,8,12,15-18,23,25,26,30,31]; the electronic structure of these systems, notably the role of the dithiolene ligands in the redox processes, has been probed by ab initio and density functional calculations [21,32].

There are a range of strategies available to synthesize dithiolene complexes [33]. We have adapted the procedure developed by Davies et al. [34,35] to synthesize four new $[Au(dithiolene)_2]^-$ complexes, each of which involves the metal coordinated by two asymmetrically substituted dithiolenes.

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2. Experimental

Anhydrous *N*,*N*-dimethylformamide (DMF), over molecular sieves, was purchased from Fluka and used as received. Potassium *O*-isopropyl xanthate [36], 4-(phenyl)-1,3-dithiol-2-one [37], 2-bromoacetylpyridine hydrobromide, 3-bromoacetylpyridine hydrobromide and 4-bromoacetylpyridine hydrobromide [38,39] were prepared by the literature methods or modifications thereof.

2.1. Synthesis of 4-(pyridin-2-yl)-1,3-dithiol-2-one

2–Bromoacetylpyridine hydrobromide (8.41 g, 29.9 mmol) was suspended in CH_2Cl_2 (60 cm³) and triethylamine (3.64 g, 36.0 mmol) added to give a pink solution. Potassium O-isopropyl xanthate (6.26 g, 36.0 mmol) was added and the orange suspension stirred for 2 h. The reaction was quenched by the addition of water (100 cm³) and the CH_2Cl_2 layer separated. The aqueous phase was washed with CH_2Cl_2 (2 × 10 cm³), the CH_2Cl_2 phases were combined, dried (MgSO₄), filtered, and the filtrate evaporated in vacuo to give a brown solid. The solid was treated with H_2SO_4 $(10 \text{ cm}^3, 98\%)$ resulting in an exothermic reaction. After 5 min, ice was added to the reaction until no further heat was generated. The solution was diluted with water and then neutralised with NaHCO₃. The pale precipitate was extracted into CH2Cl2, the organic phase dried (MgSO4), and the filtrate evaporated to dryness to yield a pale brown solid. Recrystallization from hot EtOH afforded a cream colored solid (0.80 g, 14%). Elemental Anal. Calc. for C₈H₅NOS₂: C, 49.27; H, 2.58; N, 7.18. Found: C, 49.18; H, 2.57; N, 6.98%. EI-MS *m*/*z*: 195 (C₈H₅NOS₂⁺), 167 (C₇H₅NS₂⁺), 123 (C₆NSH₅⁺), 78 (C₅H₄N⁺). ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3, 298 \text{ K}): \delta_H 8.60-8.58 \text{ (m, 1H, H}^6),$ 7.79–7.73 (m, 1H, H³), 7.53–7.50 (m, 1H, H⁴), 7.36 (s, 1H, H^{dithio}), 7.28–7.24 (m, 1H, H⁵).

2.2. Synthesis of 4-(pyridin-3-yl)-1,3-dithiol-2-one

This compound was prepared as for 4-(pyridin-2-yl)-1,3dithiol-2-one from 3-bromoacetylpyridine hydrobromide (8.11 g, 28.9 mmol), triethylamine (3.51 g, 34.8 mmol), potassium *O*-isopropyl xanthate (6.06 g, 34.8 mmol) and H₂SO₄ (10 cm³, 98%), and obtained as a cream colored solid 0.90 g (16%). Elemental *Anal*. Calc. for C₈H₅NOS₂: C, 49.27; H, 2.58; N, 7.18. Found: C, 49.26; H, 2.52; N, 7.18%. EI-MS *m*/*z*: 195 (C₈H₅NOS₂⁺), 167 (C₇H₅NS₂⁺), 122 (C₆NSH₄⁺), 78 (C₅H₄N⁺). ¹H NMR (300 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ 8.73–8.72 (m, 1H, H²), 8.63–8.60 (m, 1H, H⁶), 7.73–7.69 (m, 1H, H⁴), 7.38–7.33 (m, 1H, H⁵), 6.94 (s, 1H, H^{dithio}).

2.3. Synthesis of 4-(pyridin-4-yl)-1,3-dithiol-2-one

This compound was prepared as for 4-(pyridin-2-yl)-1,3dithiol-2-one from 4-bromoacetylpyridine hydrobromide (7.63 g, 27.2 mmol), triethylamine (3.30 g, 32.7 mmol), potassium *O*-isopropyl xanthate (5.57 g, 32.0 mmol) and H₂SO₄ (10 cm³, 98%), and obtained as a cream colored solid (1.14 g, 22%). Elemental *Anal*. Calc. for C₈H₅NOS₂: C, 49.27; H, 2.58; N, 7.18. Found: C, 48.88; H, 2.52; N, 6.97%. EI-MS *m/z*: 195 (C₈H₅NOS₂⁺), 167 (C₇H₅NS₂⁺), 122 (C₆NSH₄⁺), 78 (C₅H₄N⁺). ¹H NMR (300 MHz, CDCl₃, 298 K): $\delta_{\rm H}$ 8.67 (dd, 2H, H², H⁶, *J*_{H-H} 4.5, 1.7 Hz), 7.30 (dd, 2H, H³, H⁵, *J*_{H-H} 4.4, 1.6 Hz), 7.15 (s, 1H, H^{dithio}).

2.4. Synthesis of $[PPh_4][Au(sdt)_2]$ (1)

4-Phenyl-1,3-dithiol-2-one (0.10 g, 0.5 mmol) and NaOH (0.10 g, 2.5 mmol) were suspended in EtOH (10 cm^3) . A solution of K[AuCl₄] (0.10 g, 0.3 mmol) in water (10 cm³) was added and a dark yellow colored solution was obtained. This solution was heated at reflux for 3 h and then allowed to cool to room temperature. A solution of $[PPh_4]Br$ (0.20 g, 0.5 mmol) in water (10 cm³) was then added and a pale brown solid precipitated. The volume of the solvent was reduced in vacuo and the precipitate collected by filtration. This solid was recrystallized from a CH₂Cl₂ solution layered with *n*-hexane; the product was isolated by decantation of the mother liquor and then dried in vacuo to yield a golden crystalline solid (0.11 g, 51%). Elemental Anal. Calc. for AuS₄PC₄₀H₃₂: C, 55.29; H, 3.71. Found: C, 54.35; H, 3.69%. FAB-MS m/z: 530 $[Au(sdt)_2]^{-1}$. ¹H NMR (300 MHz, (CD₃)₂CO, 298 K): δ_{H} 8.03-7.94 (m, 4H, PPh₄), 7.88-7.82 (m, 16H, PPh₄), 7.57 $(m, 4H, H^2, H^6), 7.19 (m, 4H, H^3, H^5), 7.08 (m, 2H, H^4),$ 6.63, 6.62 (2s, 2H, H^{dithio}).

2.5. Synthesis of $[PPh_4][Au(2-pedt)_2]$ (2)

This compound was prepared as described for 1 from 4-(pyridin-2-yl)-1,3-dithiol-2-one (0.10 g, 0.5 mmol), NaOH (0.10 g, 2.5 mmol) and K[AuCl₄] (0.10 g, 0.3 mmol). Addition of a solution of [PPh₄]Br (0.20 g, 0.5 mmol) in water (10 cm^3) to the dark yellow solution resulted in the precipitation of a pale brown solid. The volume of the solvent was reduced in vacuo, the precipitate was collected by filtration and then recrystallized from a solution in CH₂Cl₂ layered with *n*-hexane. The product was isolated by decantation of the mother liquor and then dried in vacuo to yield a golden crystalline solid (0.04 g, 18%). Elemental Anal. Calc. for AuS₄N₂PC₃₈H₃₀: C, 52.41; H, 3.47; N, 3.22. Found: C, 52.21; H, 3.34; N, 3.04%. FAB-MS m/z: 532 $[Au(2-pedt)_2]^-$. ¹H NMR (300 MHz, (CD₃)₂CO, 298 K): $\delta_{\rm H}$ 8.32 (m, 2H, H⁶), 8.03–7.96 (m, 4H, PPh₄), 7.89–7.81 (m, 16H, PPh₄), 7.62, 7.61 (2s, 2H, H^{dithio}), 7.60-7.58 (m, 4H, H³, H⁴), 6.99 (m, 2H, H⁵).

2.6. Synthesis of $[PPh_4][Au(3-pedt)_2](3)$

This compound was prepared as described for 1 from 4-(pyridin-3-yl)-1,3-dithiol-2-one (0.10 g, 0.5 mmol), NaOH (0.10 g, 2.5 mmol) and K[AuCl₄] (0.10 g, 0.3 mmol).

Addition of a solution of $[PPh_4]Br (0.20 \text{ g}, 0.5 \text{ mmol})$ in water (10 cm³) to the dark yellow solution resulted in the precipitation of a pale brown solid. The volume of the solvent was reduced in vacuo, the precipitate was collected by filtration and then recrystallized from a solution in CH₂Cl₂ layered with *n*-hexane. The product was isolated by decantation of the mother liquor and then dried in vacuo to yield a golden crystalline solid (0.08 g, 37%). Elemental *Anal.* Calc. for AuS₄N₂PC₃₈H₃₀: C, 52.41; H, 3.47; N, 3.22. Found: C, 52.26; H, 3.49; N, 3.10%. FAB-MS *m/z*: 532 [Au(3-pedt)₂]⁻. ¹H NMR (300 MHz, (CD₃)₂CO, 298 K): $\delta_{\rm H}$ 8.80 (d, 2H, H², *J*_{H-H} 2.1 Hz), 8.30 (dd, 2H, H⁶, *J*_{H-H} 4.9, 1.6 Hz), 8.03–7.97 (m, 4H, PPh₄), 7.89–7.83 (m, 18H, PPh₄, H⁴), 7.19 (m, 2H, H⁵) 6.79, 6.78 (2s, 2H, H^{dithio}).

2.7. Synthesis of $[PPh_4][Au(4-pedt)_2]$ (4)

This compound was prepared as described for 1 from 4-(pyridin-4-yl)-1,3-dithiol-2-one (0.10 g, 0.5 mmol), NaOH (0.10 g, 2.5 mmol) and K[AuCl₄] (0.10 g, 100 g)0.3 mmol). Addition of a solution of [PPh₄]Br (0.20 g, 0.5 mmol) to the dark yellow solution resulted in the precipitation of a pale brown solid. The volume of the solvent was reduced in vacuo, the solid was separated by filtration and then recrystallized from a solution in CH_2Cl_2 layered with *n*-hexane. The product was isolated by decantation of the mother liquor and then dried in vacuo to yield a golden crystalline solid (0.04 g, 18%). Elemental Anal. Calc. for AuS₄N₂PC₃₈H₃₀: C, 52.41; H, 3.47; N, 3.22. Found: C, 51.99; H, 3.48; N, 3.15%. FAB-MS *m/z*: 532 [Au(4-pedt)₂]⁻. ¹H NMR (300 MHz, $(CD_3)_2CO, 298 \text{ K}$: $\delta_H 8.36 \text{ (dd, 4H, H}^2, H^6, J_{H-H} 4.7,$ 1.6 Hz), 8.03-7.94 (m, 4H, PPh₄), 7.89-7.83 (m, 16H, PPh₄), 7.49 (dd, 4H, H³, H⁵, J_{H-H} 4.9, 1.6 Hz), 7.15, 7.14 (2s, 2H, H^{dithio}).

3. Physical characterization

Elemental analyses of the compounds isolated in these studies were accomplished by the Microanalytical Laboratory of the School of Chemistry, the University of Nottingham, and by the Elemental Analysis Service at London Metropolitan University. FAB and EI mass spectra were recorded on a Fisons VG Trio 200 or a Fisons VG Autospec spectrometer. ¹H NMR spectra were recorded on a Bruker DPX300 NMR spectrometer and UV/Vis spectra were recorded on a Perkin–Elmer Lambda 16 spectrophotometer.

The cyclic voltammogram of each compound (1 mM) in DMF, containing [NⁿBu₄][BF₄] (0.2 M) as the background electrolyte, was recorded at room temperature using a glassy carbon working electrode, a Pt wire secondary electrode, and a saturated calomel reference electrode. To avoid overlapping redox couples, the $[(Me_5C_5)_2Fe]^+/[(Me_5C_5)_2Fe]([Fc^*]^+/[Fc^*])$ couple was used as the internal reference and the potentials of the redox processes observed were referenced to that of the $[Fc]^+/[Fc]$ couple by an independent calibration ($\Delta E_{1/2}$, $[Fc]^+/[Fc]$ versus $[Fc_2^*]^+/[Fc_2^*]$, = 0.475 V). Measurements were performed using an Autolab PGSTAT20 potentiostat and compensation for internal resistance was not applied.

Golden, single crystals of 1, 2, 3 and 4 were grown by dissolution of the corresponding compound in CH₂Cl₂ followed by the slow diffusion of *n*-hexane into the solution. Details of the unit cell dimensions, data collection, and refinement are given in Table 1. Data for the structures of 1, 2 and 3 were collected on a Bruker SMART 1000 CCD area detector diffractometer, whilst data for 4 were collected on a Bruker SMART APEX detector diffractometer. Both systems were equipped with an Oxford Cryosystems open flow cryostat. Structures 1 and 2 were solved by direct methods and structures 3 and 4 by Patterson heavy-atom

Table 1

Unit cell dimensions, data collected and refined for the crystal structures of $[PPh_4][Au(sdt)_2]$ (1), $[PPh_4][Au(2-pedt)_2]$ (2), $[PPh_4][Au(3-pedt)_2]$ (3), and $[PPh_4][Au(4-pedt)_2]$ (4)

Compound	1	2	3	4	
Empirical formula	C ₄₀ H ₃₂ Au P S ₄	C ₃₈ H ₃₀ Au N ₂ P S ₄	C ₃₈ H ₃₀ Au N ₂ P S ₄	C ₃₈ H ₃₀ Au N ₂ P S ₄	
Μ	868.83	870.82	870.82	870.82	
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	
Space group	$P2_1/n$	$P2_1/n$	I2/a	I2/a	
a (Å)	14.7438(11)	14.3534(8)	18.187(4)	18.169(2)	
b (Å)	13.7638(10)	13.8681(7)	17.332(4)	17.452(2)	
c (Å)	17.0507(13)	17.0646(9)	21.346(5)	21.532(2)	
α (°)	90	90	90	90	
β (°)	92.199(2)	91.873(1)	90.960(4)	94.417(2)	
γ (°)	90	90	90	90	
$V(\text{\AA}^3)$	3457.6(4)	3395.0(5)	6728(3)	6807(2)	
Z	4	4	8	8	
$\mu ({\rm mm^{-1}})$	4.572	4.658	4.701	4.646	
Reflections collected	30951	19494	20743	19270	
Independent reflections	8584	8226	8115	7918	
R _{int}	0.032	0.038	0.062	0.033	
Final R_1 [$I \ge 2\sigma(I)$], wR_2	0.0264, 0.0571	0.0344, 0.0803	0.0540, 0.135	0.0473, 0.115	

methods, using SHELXS-97 [40]. In each case, a full-matrix least-squares refinement was carried out using SHELXL-97 [41]. All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$, unless otherwise stated. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps), except partially occupied atoms of 2 and 4. Compound 2 had a disorder in the pyridine ring containing the atoms C13-C18. The initial refined values of the isotropic adp (U_{iso}) suggested a misassignment of the carbon and nitrogen atoms C18 and N2. However, further investigation suggested an electron density intermediate between C and N at both sites. Therefore, the ring was modeled with two coincident half-occupied sites, with attendant half-occupied hydrogen atom positions corresponding to those of the C atoms. Compound 4 had a disorder in the anion containing Au2. All atoms of this anion, except the gold and sulfur, were positioned in two sites with occupancies of 0.70 and 0.30. Geometric restraints were applied to the distances in all the partial occupancy disorder models, such that the bond lengths were restrained to be the same in each component. Hydrogen atoms were geometrically placed.

4. Results and discussion

4.1. Syntheses

Each of the $[Au(SC(H)C(R)S)_2]^-$ (R = phenyl, pyridin-2-yl, pyridin-3-yl, or pyridin-4-yl: dithiolene abbreviations = sdt, 2-pedt, 3-pedt, and 4-pedt, respectively) complexes have been prepared (Scheme 1) by reacting K[AuCl₄] with the appropriate dithiolene, generated by base hydrolysis of the corresponding thione-protected 1,3-dithiolate. Each [Au-(SC(H)C(R)S)₂]⁻ complex has been isolated as its [PPh₄]⁺ salt (compounds **1**, **2**, **3**, and **4**, respectively) in a reasonable (18–51%) yield.

4.2. Structural information

The asymmetric unit of compounds 1 and 2 each comprises a $[PPh_4]^+$ cation and a $[Au(dithiolene)_2]^-$ (dithio-



Scheme 1. Route used for the synthesis of $[PPh_4][Au(dithiolene)_2]$ (dithiolene = SC(H)C(R)S, R = phenyl (sdt), pyridin-2-yl (2-pedt), pyridin-3-yl (3-pedt) and pyridin-4-yl (4-pedt)) compounds. The numbering scheme for the various ligand substituents has been used in the assignment of the ¹H NMR spectra of these compounds.

lene = sdt or 2-pedt) anion, each of which has a *cis*configuration (Fig. 1(a) and (b)). The asymmetric unit of compounds **3** and **4** each comprises a $[PPh_4]^+$ cation and two independent half $[Au(dithiolene)_2]^-$ (dithiolene = 3pedt or 4-pedt) anions, the Au atoms of which are situated on an inversion center, i.e., each anion has a *trans*-configuration (Fig. 1(c) and (d)). The dimensions of each $[Au(dithiolene)_2]^-$ complex are presented in Table 2. In each anion, the AuS₄ center is essentially square planar: the length of the four Au-S bonds is essentially the same (2.30 ± 0.02 Å); the S–Au–S angles are all close to 90°; and the AuS₄ array is precisely planar in compounds **3**



Fig. 1. Structure of: (a) $[Au(sdt)_2]^-$; (b) $[Au(2-pedt)_2]^-$; (c) $[Au(3-pedt)_2]^-$; and (d) $[Au(4-pedt)_2]^-$ in the corresponding $[PPh_4][Au(dithiolene)_2]$ compound (1, 2, 3 and 4, respectively).

Table 2 Dimensions (bond length/Å; interbond angle/°) of the $[Au(dithiolene)_2]^-$

(3) and $[PPh_4][Au(4-pedt)_2]$ (4)							
Structure	1	2	3	4			
Au1–S1	2.3126(9)	2.3124(12)	2.297(2)	2.308(2)			
Au1–S2	2.3141(9)	2.3173(12)	2.298(2)	2.3054(18)			
Au(A)–S3	2.3199(9)	2.3083(12)	2.301(2)	2.311(2)			
Au(A)–S4	2.3149(9)	2.3116(12)	2.299(2)	2.2817(19)			
S1-C1	1.737(4)	1.732(4)	1.732(9)	1.741(8)			
S2-C2	1.777(3)	1.768(5)	1.770(8)	1.777(8)			
S3-C11	1.744(3)	1.732(5)	1.730(9)	1.766(8)			
S4-C12	1.770(3)	1.769(4)	1.759(9)	1.749(8)			
C1–C2	1.336(5)	1.335(6)	1.349(10)	1.335(10)			
C11–C12	1.337(4)	1.343(7)	1.337(12)	1.343(16)			
S1-Au1-S2	89.66(3)	89.80(4)	89.95(8)	89.97(7)			
S3-Au(A)-S4	89.95(3)	89.90(4)	89.62(8)	90.00(8)			
Au1-S1-C1	101.15(12)	101.25(17)	101.7(3)	101.6(3)			
Au1-S2-C2	102.32(11)	101.59(15)	102.6(3)	102.1(2)			
Au(A)-S3-C11	100.82(12)	101.39(15)	101.4(3)	98.4(5)			
Au(A)-S4-C12	101.82(10)	101.71(17)	102.8(3)	105.2(5)			
S1-C1-C2	126.2(3)	125.4(4)	125.4(6)	125.1(6)			
S2-C2-C1	120.3(3)	121.7(4)	120.3(7)	121.3(6)			
S3-C11-C12	125.6(3)	125.2(4)	125.7(7)	129.1(10)			
S4-C12-C11	121.3(2)	121.3(4)	120.4(7)	116.2(10)			

anions of [PPh₄][Au(sdt)₂] (1), [PPh₄][Au(2-pedt)₂] (2), [PPh₄][Au(3-pedt)₂]

The labelling of the atoms is shown in Figure 1 and Au(A) corresponds to Au(1) for 1 and 2 (the asymmetric unit of which involve one [Au(dithio-lene)_2]⁻ anion) and Au(2) for 3 and 4 (the asymmetric unit of which involve two independent half [M(dithiolene)_2]⁻ anions).

and **4** and very close to planar in compounds **1** and **2** (the maximum deviation of an atom from the AuS₄ plane is 0.044 Å in **1** and 0.043 Å in **2**). Also, each {AuSCCS} metallodithiolene ring is essentially planar with the maximum displacement from the mean plane being ≤ 0.05 Å. These structural details are in good agreement with those reported for other [Au(dithiolene)₂]⁻ anions [6,9,13, 16,19,20,22,29–31], as are the C–S (1.75 ± 0.03 Å) and dithiolene C–C (1.34 ± 0.01 Å) bond lengths (provided that the C–C bond is not part of an aromatic ring).

The four crystal structures described herein are the first such examples of gold bound to two asymmetrically substituted dithiolenes; also, $[Au(sdt)_2]^-$ and $[Au(2-pedt)_2]^-$ represent the first *cis*-isomers of a bis-dithiolene complex to be structurally characterized. The essential equivalence of the four M–S and four C–S bonds of each $[Au(dithiolene)_2]^-$ (dithiolene = sdt, 2-pedt, 3-pedt, or 4-pedt) complex indicates that the asymmetric nature of the dithiolene does not significantly affect the nature of the metal–sulfur interactions. However, the asymmetric nature of the dithiolene ligands *is* reflected in the S–C–C interbond angles; the S–C(H)–C(R) angles (125.1(6)–126.2(3)°) are significantly larger than the S–C(R)–C(H) angles (116.2(10)–121.7(4)°).

An important aspect to the nature of a dithiolene complex is the "non-innocence" of this ligand, the two extreme forms being the ene-1,2-dithiolate ($^{S}-C=C-S^{-}$) and the dithioketone (S=C-C=S) [42]. Thus, the lengths of the C–C and C–S bonds can be used to comment on the nature of a dithiolene ligand in a complex, especially when – as in

the present cases – the dithiolene ring is not fused to an aromatic ring. For sp^2 hybridized carbon atoms, typical bond lengths are: C-C, 1.43-1.48 Å; C=C, 1.30-1.36 Å; C-S, 1.71-1.75 Å; and C=S 1.67-1.68 Å [43]. Thus, the length of both the C–C $(1.34 \pm 0.01 \text{ Å})$ and the C–S $(1.75 \pm 0.03 \text{ Å})$ bonds of the ligands in each of the compounds 1-4 are consistent with the ene-1,2-dithiolate form of the dithiolene. Therefore, these $[Au(dithiolene)_2]^-$ anions can, to a first approximation, be formulated as Au(III) bis(ene-1,2-dithiolate) complexes, as proposed for [Au(1,2- $C_6H_4S_2_2$ by Ray et al. on the basis of the C-S bond lengths of this complex (average 1.762 A) [31]. Consistent with this proposal, the electronic spectrum of compound 1 contains two weak absorptions at ca. 720 nm $(\varepsilon \sim 100 \text{ M}^{-1} \text{ cm}^{-1})$ and ca. 465 nm $(\varepsilon \sim 260 \text{ M}^{-1} \text{ cm}^{-1})$, similar to those of $[Au(1,2-C_6H_4S_2)_2]^-$ and related $[Au(dithiolene)_2]^-$ complexes [21,31].

4.3. ¹H NMR spectroscopy

The dithiolene proton of these $[Au(SC(H)C(R)S)_2]^{-1}$ complexes provides a valuable probe of the nature of these complexes in solution. In the ¹H NMR spectrum of each $[PPh_4][Au(dithiolene)_2]$ (dithiolene = sdt, 2-pedt, 3-pedt, or 4-pedt) compound in (CD₃)₂CO at 298 K the dithiolene (H^{dithio}) resonances were observed as two singlets, consistent with the presence of both cis and trans isomers of the square-planar anion in solution. The resonances observed and the ratio of the integrals were: [PPh₄][Au(sdt)₂], 6.63 and 6.62 ppm, ca. 1:1; [PPh4][Au(2-pedt)2], 7.62 and 7.61 ppm, ca. 1:1; [PPh₄][Au(3-pedt)₂], 6.79 and 6.78 ppm, ca. 9:1; and [PPh₄][Au(4-pedt)₂], 7.16 and 7.15, ca. 1:1. These H^{dithio} resonances vary with the nature of the dithiolene as 2-pedt > 4-pedt > 3-pedt > sdt, as observed for the $[MO(dithiolene)_2]^{2-}$ (M = Mo or W) complexes of these ligands. This order is consistent with nature of the ligands, in respect of: (i) inductive effects and (ii) the relative ability of the aromatic substituent to stabilize a resonance form in which a positive charge is localized at the C atom carrying the dithiolene proton [34,35].

The resolution of two environments for the dithiolene protons of compounds 1-4 contrasts with the ¹H NMR spectra observed for [Ni(sdt)₂], in CD₂Cl₂; at >198 K a single dithiolene resonance is manifest but, at 198 K two resonances, of relative intensity ca. 1:1 and separated by 9.8 Hz are resolved. This latter information is consistent with a rapid interconversion of the cis and trans isomers of [Ni(sdt)₂] at >198 K and has been attributed to a facile rotation of the ligand(s) around the metal [44]. Noting these results, the ¹H NMR spectrum of [PPh₄][Au(sdt)₂] in (CD₃)₂SO was recorded at ca. 298, 320, 330, 340, 355 and 365 K. At each temperature, the dithiolene proton resonances appeared as two singlets with a relative intensity of ca. 1:1. The splitting between these two singlets decreased slightly as the temperature was increased, from 3.28 Hz at 298 K to 2.96 Hz at 365 K, suggesting that coalescence may occur at >365 K. However, it is clear that the

activation energy for the interconversion of the *cis* and *trans* isomers of $[Au(sdt)_2]^-$ is significantly greater than that for the corresponding process of $[Ni(sdt)_2]$ [44]; this could be due to stronger metal–ligand bonds for Au (a 5d-metal) than Ni (a 3d-metal).

The presence of essentially equal amounts of the *cis* and *trans* isomers of $[Au(sdt)_2]^-$, $[Au(2-pedt)_2]^-$, and $[Au(4-pedt)_2]^-$ in solution and the lack of any significant interconversion of these isomers at room temperature suggests that solid samples of their $[PPh_4]^+$ salts contain an essentially equal amounts of the two isomers. However, from the structural studies, it appears that one isomer of the anion may preferentially crystallize and/or been present in the crystal selected for X-ray analysis. In respect of $[PPh_4]$ - $[Au(3-pedt)_2]$, we presume that the *trans* isomer identified by X-ray crystallography predominates in the sample for which the ¹H NMR spectrum was recorded.

4.4. Redox behavior

The cyclic voltammogram of each [PPh₄][Au(dithiolene)₂] (dithiolene = sdt, 2-pedt, 3-pedt, or 4-pedt) compound has been recorded in dmf solution containing [NⁿBu₄][BF₄] (0.2 M) as the background electrolyte. Each compound (Table 3) exhibits both an oxidation and a reduction process.

The oxidation of the compounds 1–4 occurs in the range $80 \text{ mV} < E_p^a(\text{ox}) < 230 \text{ mV}$ (versus [Fc]⁺/[Fc]). The relative values of these potentials (Table 3) correlates with the electron withdrawing nature of the substituent (R), as measured by the Hammett parameter, σ_p [45]; thus, 1 (R = Ph; $\sigma_{\rm p} = -0.01$) is the easiest to oxidize ($E_{\rm p}^{\rm a}({\rm ox}) =$ 80 mV) and 4 (R = pyridin-4-yl; $\sigma_p = 0.44$) is the most difficult to oxidize $(E_p^a(ox) = 230 \text{ mV})$. For each compound 1–4, a variation in the scan rate (from 20 to 300 mV s^{-1}), monitoring the wave profile, the separation of the peak potentials (ΔE generally >70 mV), and the ratio of the cathodic and anodic currents $(-I_p^c: I_p^a \neq 1.0)$ indicated that the oxidation is not electrochemically reversible. The most promising results were obtained for compound 1 (Fig. 2). At a scan rate $>50 \text{ mV s}^{-1}$, ΔE is ca. 70 mV and comparable with that of the $[Fc^*]^+/[Fc^*]$ couple used as

Table 3

Potentials (vs. $[Fc]^+/[Fc]$) observed for the oxidation and reduction of $[PPh_4][Au(sdt)_2]$ (1), $[PPh_4][Au(2-pedt)_2]$ (2), $[PPh_4][Au(3-pedt)_2]$ (3), and $[PPh_4][Au(4-pedt)_2]$ (4) (1 mM) at room temperature in DMF containing $[N^nBu_4][BF_4]$ (0.2 M)

Compound	$E_{\rm p}^{\rm a}({\rm ox})$	$E_{1/2}(\mathrm{ox})$	$E_{\rm p}^{\rm c}({\rm red})$	$E_{1/2}(\text{red})$	$\Delta E([Fc^*]^+/[Fc^*])$
1	80	50(70)	-2020	-1970(90)	70
2	120		-1970	-1920(90)	80
3	180		-1920	-1880(90)	70
4	230	200(70)	-1880	-1840(90)	70

The shape of the voltammogram observed for the oxidation of **2** and **3** does not allow an accurate determination of $E_{1/2}$. For each compound, other redox processes were observed outside the potential range 1000 to -2100 mV.



Fig. 2. Cyclic voltammogram of $[PPh_4][Au(sdt)_2]$ (1) (1 mM), at room temperature in DMF containing $[N^nBu_4][BF_4]$ (0.2 M), recorded using a glassy carbon working electrode, a Pt wire secondary electrode, and a saturated calomel reference electrode; potentials are vs. the $[Fc]^+/[Fc]$ couple.

an internal standard. Also, the oxidation was monitored by UV/Vis spectroscopy and the profile seen to change through a series of isosbestic points. However, application of a potential sufficient to reverse the oxidation did not reproduce the original UV/Vis spectrum (even at 243 K). Therefore, the product of the oxidation of 1 is not stable within the timescale of the bulk electrolysis experiment. Also, oxidation of 1 with I_2 did not produce a stable product.

The reduction of the compounds 1-4 occurs in the range $-1880 \text{ mV} < E_p^c(\text{red}) < -2020 \text{ mV} \text{ (versus } [Fc]^+/[Fc]).$ As for oxidation of these compounds, the relative values of these reduction potentials (Table 3) correlate with the electron withdrawing nature of the dithiolene substituent (R), as measured by the Hammett parameter, σ_p [45]; thus, 1 is the most difficult to reduce $(E_p^c(\text{red}) = -2020 \text{ mV})$ and **4** is the easiest to reduce $(E_p^c(\text{red}) = -1880 \text{ mV})$. For each compound the reduction wave is accompanied by a corresponding oxidation wave upon reversal of the potential (Fig. 2). The electrochemical characteristics of the process were examined for a range of scan rates $(20-300 \text{ mV s}^{-1})$ and, in each case, the reduction was not reversible. Also, following the reduction of each compound, scans at a more positive potential revealed other, relatively minor, oxidation processes, suggesting that each reduced species is reactive and/or unstable.

The cyclic voltammogram (CV) of **1** (Fig. 2) is remarkably similar, in respect of both the overall profile and the potentials of the redox processes, to the CV of $[Au(3,5-di-tert-butyl-1,2-benzenedithiolate)_2]^-$ ($[Au(3,5-(^{t}Bu)_2bdt)_2]^-$) [31]. This latter complex, in CH₂Cl₂ solution, undergoes two, reversible, one-electron processes; an oxidation at 74 mV and a reduction at -2280 mV (versus $[Fc]^+/[Fc]$). The correspondence in redox behavior and the one-electron nature of both redox couples of $[Au(3,5-(^{t}Bu)_2bdt)_2]^-$ implies that oxidation of **1** involves the $[Au(dithiolene)_2]/[Au(dithiolene)_2]^-$ couple and reduction involves the $[Au(dithiolene)_2]^-/[Au(dithiolene)_2]^{2-}$ couple.

The nature of the frontier orbitals of $[Au(dithiolene)_2]^{-1}$ complexes has been investigated by performing ab initio calculations for [Au(bdt)₂]⁻ [21] and the results of density functional calculations for $[Au(bdt)_2]^z$ (z = 0 or 1) and related complexes of Ni, Pd, Pt, and Cu [32]. Schiødt et al. [21] showed that, as observed by Schultz et al. [12], the two highest occupied molecular orbitals (HOMOs) of $[Au(bdt)_2]^-$ have π -character and comprise the antisymmetric and symmetric combination of the ligand HOMOs with 4 and 0% contribution from Au orbitals, respectively; each of these orbitals is C-S antibonding and C-C bonding in character. The LUMO of $[Au(bdt)_2]^-$ has σ -character, is the antibonding combination of the metal d_{xy} and ligand 1b_{1g} orbitals with significant contributions from both the metal (Au d_{xy} ca. 48%) and the ligand orbitals [21]. Similar results were obtained by density functional calculations accomplished for $[\operatorname{Au}(\operatorname{bdt})_2]^z$ (z = 0 or 1) [32].

As described in 4.2, the length of the C-C and C-S bonds of the dithiolene ligands of compounds 1-4 are consistent with formulation as [Au(III)(ene-1,2-dithiolate)₂]⁻, as indicated by structural [31] and theoretical [32] studies of $[Au(bdt)_2]^-$. One-electron oxidation of a [Au(dithio $lene)_2$ complex, electrochemically or chemically (e.g., I_2), yields the corresponding, paramagnetic, [Au(dithiolene)₂] complex, examples of which have been structurally characterized [12,16,30]. Dautel et al. [30] and Ray et al. [31] have compared the dimensions of a [Au(dithiolene)₂]⁻ complex with those of its a $[Au(dithiolene)_2]$ counterpart and shown that conversion of the former to the latter leaves the Au-S bond length essentially unchanged, but the C-S bond shortens and the C-C bond lengthens. These structural changes are consistent with the loss of an electron from the HOMO of a [Au(dithiolene)₂]⁻ complex, i.e., this ligand-based orbital¹ is Au-S non-bonding, C-S antibonding, and C–C bonding [21,32].

One-electron reduction of a $[Au(dithiolene)_2]^-$ complex yields the corresponding $[Au(dithiolene)_2]^{2-}$ complex that possesses one unpaired electron and EPR spectra of several of these systems have been reported [2,7,8,25,26]. A singlecrystal EPR-ENDOR study of ¹³C enriched $[^nBu_4$. N]₂[Au(mnt)₂] diluted in $[^nBu_4N]_2[Ni(mnt)_2]$ found that the majority (ca. 64%) of the unpaired spin density is located on the *S*-atoms [25,26]. This information is in qualitative agreement with the significant involvement of ligand orbitals in the LUMO of $[Au(dithiolene)_2]^-$ complexes [21,32]. A comparison of redox potentials for $[Au(L)_2]^-$ (L = sdt, 2-pedt, 3-pedt or 4-pedt) with those of their $[M(L)_2]^-$ (M = Ni, Pd or Pt) analogs [43] indicates that oxidation is less sensitive to a change in the metal than that of the corresponding reduction process. This is consistent with an oxidation being predominantly ligand-based and reduction involving an orbital with both ligand and metal character (vide infra). The trends within this series of $[Au(L)_2]^-$ complexes indicate a tuning of the ligand energy levels by the appended aromatic substituents.

5. Conclusions

Four new [Au(dithiolene)₂]⁻ complexes, each involving two asymmetrically substituted dithiolene ligands (SC(H)-C(R)S; R = phenyl, pyridin-2-yl, pyridin-3-yl, or pyridin-4-yl) have been synthesised, isolated as the $[PPh_4]^+$ salt and structurally characterized. The lengths of the C-C and C-S bonds of the ligands in each $[Au(dithiolene)_2]^$ complex is consistent with the dithiolene being present as an ene-1,2-dithiolate and, hence these are [Au(III)bis(ene-1,2-dithiolate)⁻ complexes. Each compound is diamagnetic and ¹H NMR studies indicate that, in solution in d⁶-acetone, both the *cis* and *trans* isomers of the $[Au(SC(H)C(R)S)_2]^-$ anion are present and do not interconvert at room temperature. Each $[Au(dithiolene)_2]^$ complex undergoes a ligand-based oxidation process and a reduction that involves the addition of an electron to an orbital that possesses considerable ligand character. These [PPh4] [Au(dithiolene)₂] compounds are suitable diamagnetic hosts that facilitate EPR studies of corresponding $[M(dithiolene)_2]^-$ (M = Ni, Pd, or Pt) complexes [46].

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Appendix A. Supplementary data

Crystallographic data for the structure of compounds 1–4 have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 275968, 275969, 275970 and 275971, respectively. Copies of the information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44 1223 336408; fax: +44 1223 336033). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.09.002.

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¹ Ray et al. [31,32] favor a description of the oxidized species as $[Au^{III}(L)(L^{\cdot})](L = dithiolene)$. This implies that oxidation of a $[Au(dithiolene)_2]^-$ complex removes an electron from *one* ligand, *whereas* the theoretical results [12,21,32] indicate that the electron is lost from an orbital that involves an equal contribution from each ligand and the dimensions observed for $[Au(dithiolene)_2]$ complexes provide no such distinction between the ligands [12,16,30].

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