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A radical mixed-ligand gold bis(dithiolene) complex†

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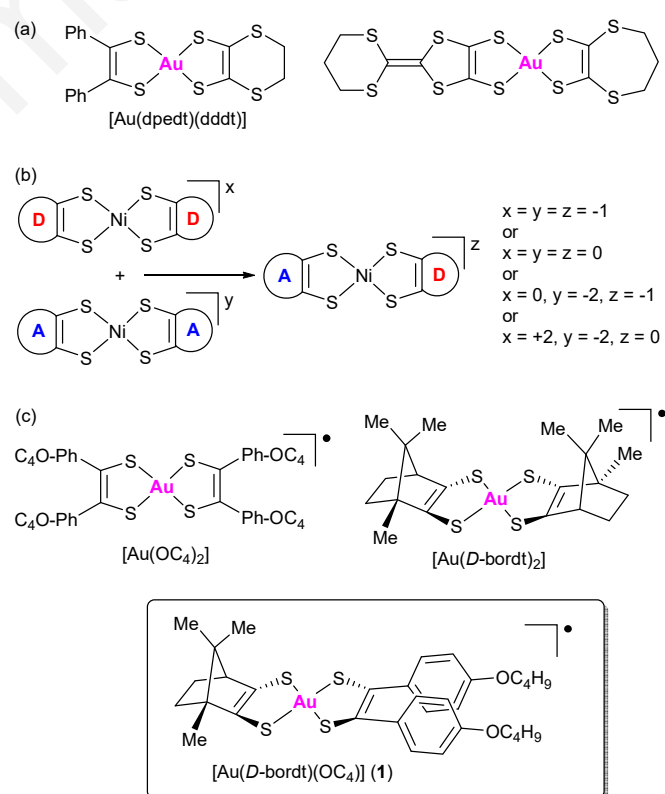
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A mixed-ligand bis(dithiolene) gold complex is isolated from scrambling reaction of two neutral radical symmetric complexes. Its asymmetric character translates into specific structural and electronic properties including larger electrochemical and optical band gaps than those of both precursors.

Dithiolene (dt) complexes have been extensively investigated since the early 1950's,¹ particularly for their involvement in biomimetic systems,² as precursors of molecular conductors,^{3,4} and for their intense NIR (Near InfraRed) absorption.⁵ Homoleptic complexes and specifically the square-planar bis(dithiolene) complexes are the most studied ones. In the electrochemical series d^8 -[Ni(dt)₂]²⁻ / [Ni(dt)₂]¹⁻ / [Ni(dt)₂]⁰, the neutral, 2e⁻-oxidized complexes [Ni(dt)₂]⁰ combine a strong NIR absorption band in the range 800–1200 nm and a good stability under irradiation, useful as laser dyes,⁶ for photothermal laser printing on thin films,⁷ or for photothermal therapy applications in the first NIR transparency window.⁸ In parallel, d⁸ monoanionic Au^{III} [Au(dt)₂]¹⁻ complexes are known to oxidize into neutral radical complexes [Au(dt)₂][•],^{9,10} and exhibit a NIR absorption at even lower energies, i.e. in the second NIR window (NIR-II: 1000–1700 nm) which has a better tissue penetration depth and a higher maximum permissive exposure value.¹¹

Among these complexes, a smaller class involves in the Ni/Pd/Pt series the so-called mixed-ligand complexes [M(dt_{push})(dt_{pull})] where two different 1,2-dithiolate ligands (dt_{push}, dt_{pull}) coordinate the metal center.¹² *Push* ligands with Electron Donating Groups (R_{EDG} = Alk, Ar, OR, NR₂) raise the energy of both the HOMO and LUMO orbitals and decrease the HOMO-LUMO gap due to a reduced interaction with metal-based atomic orbitals. *Pull* ligands, with Electron Withdrawing Groups (R_{EWG} = CN, CF₃) stabilize the most reduced forms,

providing these chromophores with 2nd-order NLO properties.^{13,14} Such mixed-ligand Ni complexes were also investigated as precursors of conducting salts.¹⁵ In that respect, it is all the more surprising that similar mixed-ligand complexes with *gold* as central metal atom are essentially unknown while they could provide a wide variety of novel complexes with attractive optical (NIR-II, NLO) or solid state properties. One example, [Au(dpdt)(dddt)], was isolated in 1% yield,¹⁶ while another example was obtained serendipitously from [Au(pdt)₂]⁻¹ (pdt: 1,2-propylenedithio-ethene-1,2-dithiolate) during its electrooxidation (Scheme 1a).¹⁷



Scheme 1 (a) Mixed-ligand bis(dithiolene) Au complexes. (b) Synthetic strategies toward mixed-ligand bis(dithiolene) Ni complexes. (c) Structure of [Au(OC₄)₂][•], [Au(D-bordt)₂][•] and mixed-ligand [Au(D-bordt)(OC₄)][•] complex **1**.

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The most successful synthetic strategy toward nickel mixed-ligand complexes is based on scrambling reactions between two preformed symmetric complexes, in the same or different oxidation states, as illustrated in Scheme 1b.¹² Difficult purification of the products however, particularly for charged complexes and/or because of competing redox reactions of the precursor complexes usually limits its applicability. Nevertheless, its adaptation to gold complexes would imply either the reaction of two d⁸, anionic complexes, or that of two oxidized, neutral radical complexes. We decided to focus on neutral radical gold complexes in principle amenable to easy purification with chromatography. The choice of soluble species is however quite restricted¹⁸ as many neutral [Au(dt)₂][•] radical complexes based on planar delocalized ligands form highly insoluble conducting materials,¹⁹ upon association into dimeric motifs or infinite stacks.^{9,10,20} We therefore chose two soluble, and stable neutral complexes we recently described (Scheme 1c), namely [Au(*D*-bordt)₂][•] (bordt = bornylene-1,2-dithiolate)²¹ and [Au(OC₄)₂][•] (OC₄ = 1,2-bis(4-butoxyphenyl)ethylene-dithiolate)²² and investigated their reaction to possibly afford the mixed-ligand [Au(*D*-bordt)(OC₄)][•] (**1**), as a proof of feasibility.

The successful preparation of **1** is based on the scrambling reaction between the two symmetric neutral radical gold complexes, namely [Au(*D*-bordt)₂][•] and [Au(OC₄)₂][•] in refluxing THF for 3 days. **1** is isolated in 33% yield after chromatographic separation and recrystallization. It is stable in CH₂Cl₂ solution without observation of ligand redistribution. Cyclic voltammetry experiments (Fig. S1) show two reversible redox processes: reduction to the anion and oxidation to the cation. As shown in Table 1, the E_{1/2} values are intermediate between those of the symmetrical compounds, with the more electron-rich [Au(*D*-bordt)₂][•] complex oxidizing at more negative potentials than [Au(OC₄)₂][•]. We note however that the potential difference ΔE = E_{1/2}(0/+1) – E_{1/2}(0/–1) actually increases in **1** relative to the values found in both symmetric complexes. This trend was not reported earlier in the nickel mixed-ligands complexes¹² within the –2/–1/0 redox series but a careful examination of published data (Table S1) shows that in mixed-ligand Ni complexes, the ΔE = E_{1/2}(–1/0) – E_{1/2}(–2/–1) values are in-between those of the symmetric complexes. The specific behaviour of the mixed-ligand gold dithiolene complex **1** is likely due to the fact that the gold atom does not contribute

Table 1 Electrochemical data. ΔE = E_{1/2}(0/+1) – E_{1/2}(–1/0). In V vs. SCE. Conditions: CH₂Cl₂, Bu₄NPF₆ 0.2 M at 100 mV/s, Pt electrodes.

Compound	E _{1/2} (–1/0)	E _{1/2} (0/+1)	ΔE	Ref
[Au(<i>D</i> -bordt) ₂] [•]	–0.05	+0.61	0.66	21
1	+0.03	+0.72	0.69	this work
[Au(OC ₄) ₂] [•]	+0.25	+0.75	0.50	22a

Table 2 EPR data for **1** and selected reference complexes.

	g _{min}	g _{int}	g _{max}	<g>	g _{max} – g _{min}	10 ^{–4} A ₀ (cm ^{–1})	Ref.
1	1.958	2.014	2.043	2.005	0.085	< 5	this work
[Au(<i>D</i> -bordt) ₂] [•]	1.963	2.017	2.052	2.011	0.089	5.8	21
[Au(OC ₄) ₂] [•]	1.945	2.026	2.059	2.010	0.114	< 5	22
[Au(^t Bu) ₂] [•]	1.944	2.030	2.065	2.013	0.121	6.6	18a
[Au(mnt) ₂] [•]	1.928	2.039	2.075	2.014	0.147	7.8	18a

significantly to the frontier orbitals.¹⁸ As a consequence, we postulate that the first oxidation of the d⁸ monoanionic [Au(dt_{push})(dt_{pull})]^{–1} complex affects preferentially the more electron-rich push ligand with a E_{1/2} value close to that of the [Au(dt_{push})₂]^{–1/0} process, while the second oxidation is concentrated on the less electron-rich pull ligand, with an E_{1/2} value closer to that of the [Au(dt_{pull})₂]^{0/+1} process, hence the notably larger ΔE value for the mixed-ligand gold complex.

As other radical gold bis(dithiolene) complexes, **1** exhibits a strong optical absorption in the NIR (Fig. S2), found at λ_{max} = 1347 nm (ε = 7 130 M^{–1} cm^{–1}). This absorption band is attributed here to a SOMO-1 → LUMO transition (Fig. S3), actually described as a HOMO → LUMO transition in neutral nickel complexes. In **1**, this absorption band (1347 nm) is found at higher energy and not in between those reported for the symmetric complexes, namely λ_{max} = 1492 nm²¹ for [Au(*D*-bordt)₂][•] and λ_{max} = 1565 nm^{22a} for [Au(OC₄)₂][•]. This striking behavior is in accordance with the larger ΔE value found in the electrochemical measurements.

The EPR signal of the radical complex **1** in a CH₂Cl₂ solution gives one single Lorentzian line with g = 2.008 and a peak-to-peak linewidth of 20.5 G (Fig. S4). Frozen solution (77 K) spectrum is typical of a rhombic system, whose characteristics are collected in Table 2, together with those of reference complexes. The absence of observable hyperfine coupling, the very small anisotropy and the g value close to that of an organic radical demonstrate that the spin density is fully delocalized on the dithiolene ligands with very small contribution from the gold center. This is a known peculiarity of neutral, radical gold bis(dithiolene) complexes,¹⁸ at variance with the isoelectronic monoanionic nickel bis(dithiolene) complexes where up to 40% of spin density is localized on the metal.²³

The chiral complex²⁴ **1** is found to crystallize in the triclinic system, space group P1, with two independent molecules in the unit cell, associated into pseudo-centrosymmetric dimers (Fig. 1). Intramolecular bond distances within the metallacycle give an indication of the degree of dissymmetry of the complex, by comparison with the same distances in both symmetric complexes [Au(*D*-bordt)₂][•] and [Au(OC₄)₂][•]. As shown in Table 3, it appears that in **1**, on the *D*-bordt side, the C–S bonds are slightly shorter and the C=C bond is slightly longer than in the symmetric [Au(*D*-bordt)₂][•] while on the OC₄ side, this weak trend is opposite, indicating that, for the mixed-ligand complex **1**, the oxidation from the d⁸ anionic species to the neutral radical state affects more the *D*-bordt (push) side than the OC₄ (pull) side. It corroborates the electrochemical properties of the complexes which indicated that the *D*-bordt complex is notably easier to oxidize (by 0.25 V) than the OC₄ complex.

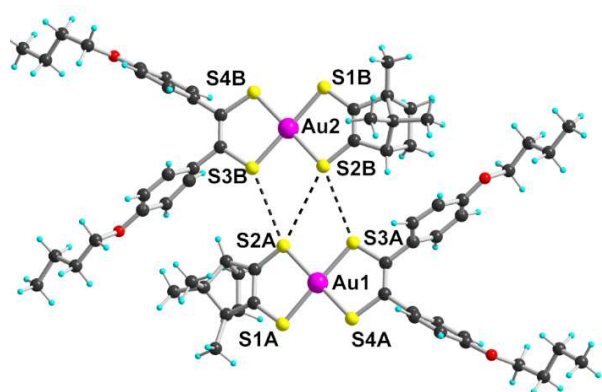


Fig. 1 The two independent molecules in **1**. The dotted lines indicate shortest S...S contacts: S2A...S3B 3.681(10) Å, S2A...S2B 3.763(11) Å, S3A...S2B 3.648(9) Å.

Note that such a dissymmetry has been pointed out previously as a characteristic of a few symmetric gold complexes, particularly those lacking extended ligand delocalization, as observed indeed to a limited extent in $[\text{Au}(D\text{-bordt})_2]^+$ itself (Fig. S5).^{9c} In **1**, this effect is strongly amplified as a direct consequence of its original mixed-ligand nature.

To get further insights on the molecular and electronic structure of **1**, DFT calculations (B3LYP/LanL2DZ, see ESI for computational details) were performed on models of **1** and of the two symmetric complexes for comparison purposes. Bond distances in the optimized geometry of the models (Table 3) confirm the trend found in the X-ray crystal structure and discussed above. Indeed, the C–S and C=C bond distances in the most e-rich *D*-bordt side of the AuS_2C_2 metallacycle in **1** show that it is more oxidized (shorter C–S and longer C=C bond distances) than in the symmetric $[\text{Au}(D\text{-bordt})_2]^+$, and conversely on the less e-rich OC_4 side. This effect is further confirmed by the spin density distribution (Fig. 4) which sums to 0.45–0.50 in both C_2S_2 fragments of the symmetric complexes while it sums to 0.87 on the *D*-bordt and 0.13 on the OC_4 side in **1**. For comparison purposes, the same geometry optimizations were conducted on the isoelectronic monoanionic nickel complexes (Table S2). The trend on bond lengths is the same, although much weaker. It is slightly more pronounced on the spin density distribution (Fig. S6), moving from 0.40–0.45 in both C_2S_2 fragments of the symmetric nickel complexes to 0.61 and 0.27 on the *D*-bordt and OC_4 sides of $[\text{Ni}(D\text{-bordt})(\text{OC}_4)]^{-1}$ respectively. This analysis confirms the specificity of the gold

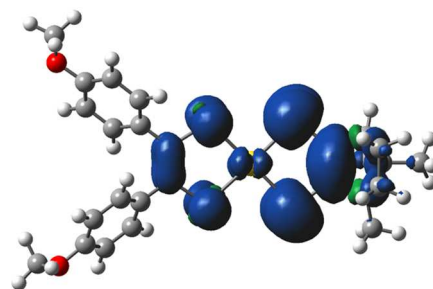


Fig. 2 Calculated spin density in **1** (cutoff: 0.02 e/bohr³).

mixed-ligand dithiolene complex, where the weak contribution of the metal centre to the frontier orbitals allows for a strong electronic separation of both dithiolene ligands, which in turn affects specifically its electrochemical/optical band gaps.

In the solid state, the complexes are associated into dimers. The shortest S...S lateral contacts, in the range 3.65–3.76 Å (Fig. 3) exceed however the van der Waals contact distance ($2 \times 1.80 = 3.60$ Å), indicating limited, if any, overlap interactions between the radical species. These dimers organize into layers (Fig. 3), without any overlap direction between the layers (Fig. S7). Consistently, magnetic susceptibility measurements show that the temperature dependence of the magnetic susceptibility (Fig. S8) is well fitted with a Curie-Weiss law with $\theta_{\text{CW}} = -11.6$ K. This behavior appears intermediate between those of the symmetric precursors. In $[\text{Au}(D\text{-bordt})_2]^+$ the steric constraints imposed by the bulky *D*-bordt ligands were shown to limit strongly antiferromagnetic interactions between radical species with a very small Curie-Weiss temperature ($\theta_{\text{CW}} = -4$ K)²¹ while in $[\text{Au}(\text{OC}_4)_2]^+$, the complexes could stack to give an alternated spin chain behaviour with $J/k = -246(1)$ K and $\alpha = 0.3$.²²

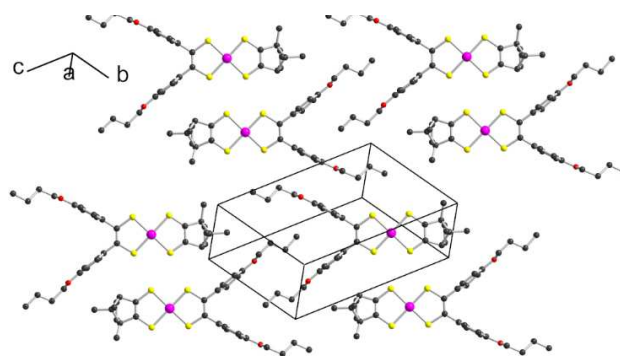


Fig. 3 A view of the layered organization of **1**.

Table 3 Averaged bond distances (Å) within the metallacycles. Numbers in italics are averaged DFT-calculated values (see text)

	<i>D</i> -bordt side			OC_4 side			Ref
	Au–S	S–C	C=C	Au–S	S–C	C=C	
$[\text{Au}(D\text{-bordt})_2]^+$	2.307(2)	1.718(12)	1.340(20)	–	–	–	21
	<i>2.461</i>	<i>1.784</i>	<i>1.372</i>				
1	2.334(5)	1.699(25)	1.368(60)	2.290(4)	1.753(5)	1.344(23)	this work
	<i>2.511</i>	<i>1.759</i>	<i>1.398</i>	<i>2.435</i>	<i>1.835</i>	<i>1.368</i>	
$[\text{Au}(\text{OC}_4)_2]^+$	–	–	–	2.306(4)	1.750(5)	1.375(5)	22a
				<i>2.450</i>	<i>1.815</i>	<i>1.386</i>	

In conclusion, we have shown that scrambling reaction between two gold bis(dithiolene) complexes, here in their neutral radical state, can successfully afford the corresponding mixed-ligand complex. At variance with isoelectronic nickel complexes, the electrochemical/optical band gaps are not intermediate but larger than those of the symmetric precursors, a consequence of the peculiar electronic structure of gold bis(dithiolene) complexes. This is also observable in the asymmetric oxidation degree of both ligands as revealed in the X-ray crystal structure of the complex. Based on the large number of known dithiolene ligands, this work opens the way to the preparation of a variety of such radical gold complexes, of strong interest for their applications as NIR dyes for photo-thermal therapy. They absorb indeed in the attractive second NIR window (1000–1700 nm). Furthermore, playing with different dithiolene ligands in mixed-ligand complexes offers the extra opportunity to effectively tune their λ_{max} absorption in an extended range, beyond that of the symmetric complexes.

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