Gold and nickel alkyl substituted bis-thiophenedithiolene complexes: anionic and neutral forms


Abstract: The Au and Ni monoanionic complexes of ter-buthyl and disopropyl substituted thiophediolate ligand \([\text{M}(\alpha\text{-tb-tpdt})_2]\) and \([\text{M}(\alpha\text{-dp-tpdt})_2]\), were synthesized and characterized namely by single crystal X-Ray diffraction and magnetic susceptibility measurements. These complexes, prepared in a first step as monoanionic species, are easier to oxidized than the related non-substituted thiophenedithiolates and could be obtained also as stable neutral species. As expected, the peripheral alkyl groups in the ligands confer also to the complexes an high solubility in common organic solvents. The neutral gold complex \([\text{Au}(\alpha\text{-tb-tpdt})_2]\) presents a significant ligand asymmetry indicative of unpaired electron localization in one ligand at variance with \([\text{Au}(\alpha\text{-dp-tpdt})_2]\), that is within experimental uncertainty fully symmetric illustrating the role of the intermolecular interactions in the stabilization of SOMO-SOMO interactions. While in \([\text{Au}(\alpha\text{-tb-tpdt})_2]\) a significant intermolecular interaction between paramagnetic molecules is possible leading to diamagnetic dimers of molecules, in \([\text{Au}(\alpha\text{-dp-tpdt})_2]\) the bulkier substituents prevent the intermolecular interactions, leading to a regular stacking of molecules in symmetrical configuration. The regular stacks of paramagnetic \([\text{Au}(\alpha\text{-dp-tpdt})_2]\) units behave at high temperatures as an antiferromagnetic chains undergoing an AFM transition at ca. 25 K.

Introduction

Transition metal bisdithiolene complexes have been a topic of intensive research during the last decades gaining increasing relevance in different fields such as materials science, analytical chemistry, catalysis and biological systems. The square planar coordination geometry of these complexes with extended π-ligands is quite favorable to establish strong face to face intermolecular interactions in the solid state. Due to significant ligand contribution to the frontier orbitals bisdithiolene complexes present a quite vivid redox behavior with diverse stable oxidation states, associated with different magnetic moments, making them choice building blocks for the preparation of conducting and magnetic molecular materials.[1][2] The discovery that some of these complexes in the neutral state can present high electrical conductivity.[3][4][5] realizing a new paradigm of molecular conductors, the so called single component metal molecular metals (SCMM), has stimulated a special interest in bisdithiolene complexes which are stable in the neutral state. However the neutral complexes tend to present relatively low solubility severely limiting the possibility of many studies namely their isolation as single crystals. This was the case of \([\text{Au}(\alpha\text{-tpdt})_2]\) (\(\alpha\text{-tpdt} = 2,3\text{-thiophenedithiolate})\), the first highly conducting metallic compound based on a neutral species with a room-temperature conductivity (\(\sigma_{RT}\)) of 7 S/cm as a polycrystalline sample, which could never be obtained as single crystals.[5] Other neutral complexes based on more extended ligands have been reported with high electrical conductivity[4][6] but due to their rather low solubility only some of them could be characterized in small single crystals as SCMM.[4]

An obvious way to increase the solubility of these complexes is the functionalization with appropriated substituents. However these substituents, particularly those more bulky can limit the solid state intermolecular interactions. This is the case of several alkyl thiazolil dithiolene complexes which due to increased solubility have been more easily obtained in the neutral state as single crystals and characterized as highly conducting materials in spite the restrains imposed by the substituents on the solid state interactions.[7][8][9] Concerning the 2,3-thiophenedithiolate ligand the substitution with methyl groups has been already described leading to complexes with a limited gain in solubility, however with poor electrical conductivity of the neutral complex characterized as a polycrystalline sample.[10]

In this paper we report the preparation of ter-buthyl and disopropyl substituted thiophediolate complexes \([\text{M}(\alpha\text{-tb-tpdt})_2]\), \([\text{M}(\alpha\text{-dp-tpdt})_2]\), \(\text{M}=\text{Au and Ni}\), \((\alpha\text{-tb-tpdt})= 5\text{-}(\text{tert-buty})\text{thiolen}[2,3\text{-d}]\text{[1,3]dithiol}) and \((\alpha\text{-dp-tpdt})= 5\text{-}6\text{-diphospho}[2,3\text{-d}]\text{[1,3]dithiol})\) obtained in stable anionic and neutral forms as well as their structural, electric and magnetic properties.

Results and Discussion

Synthesis

The key compounds for the preparation of the complexes are ketones 5-(tert-buty)thiolen[2,3-d][1,3]dithiol-2-one (II) and 5,6-dipropophyleno[2,3-d][1,3]dithiol-2-one (III), as ligand
precursors. Ketone II was prepared by a previously described Friedel-Craft alkylation of I.\textsuperscript{[11]} The ketone III was obtained by a similar procedure in a fair yield of 60%.

The monoanionic gold (1 and 3) and nickel (2 and 4) complexes based on these alkyl substitute ligands, (α-tb-tpdt) and (α-dp-tpdt), where isolated as Ph₄P⁺ salts following a common procedure usually employed for the preparation of many diothiolene complexes, which is based on the hydrolytic cleavage of ketone II and III under strictly anaerobic conditions, with sodium methoxide in methanol (Scheme 1). The free dithiolate in solution reacts subsequently with the appropriate metal chloride and Ph₄PBr, to yield the salt of the monoanionic complex. The yields range from 30-43%. These salts of monoanionic complexes are fairly soluble and were easily obtained in a crystalline form by recrystallization in dichloromethane, from where crystals suitable for x-ray single crystal analysis could be easily isolated.

The neutral complexes 5-8 were obtained by oxidation of the monoanionic complexes with iodine and single crystals suitable for x-ray single crystal could be easily obtained by slow diffusion of iodine into a solution containing the monoanionic complex.

Cyclic Voltammetry

The redox properties of these gold and nickel complexes were studied by cyclic voltammetry. The voltammograms, obtained in dichloromethane under the same conditions, for compounds 1-4, present in all cases two pairs of waves corresponding to two quasi reversible processes as shown in Figure 1. From the comparison with related bisdithiolene complexes, these waves are ascribed in case of Ni complexes, to the dianionic/monoanionic and monoanionic/neutral couples, while in the case of the Au complexes to the monoanionic/neutral, and neutral/cationic couples. The corresponding redox potentials are compared in Table 1 to those of closely related complexes.

![Scheme 1. Preparation route for alkyl substituted bis-thiophenedithiolene complexes 1-8.](image)

![Figure 1. Cyclic voltammetry of 1 (orange), 2 (green), 3 (red) and 4 (blue).](image)

From this comparison it results that the alkyl substituted dithiothiophene metal complexes are, as expected, easier to oxidize, namely to the neutral species, than the unsubstituted analogues, and in case of gold even cationic species are expected to be stable.

<table>
<thead>
<tr>
<th>Table 1. Half wave, E_{1/2}, potentials (mV) of gold and nickel complexes based on bisdithiophene ligands relative to ferrocene/ferrocenium.\textsuperscript{[10]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E'_{1/2} (mV)\textsuperscript{[II]}</td>
</tr>
<tr>
<td>Ni(α-bp-tpdt)₂</td>
</tr>
<tr>
<td>Ni(α-m-tpdt)₂</td>
</tr>
<tr>
<td>Au(α-bp-tpdt)₂</td>
</tr>
<tr>
<td>Ni(α-tb-tpdt)₂</td>
</tr>
<tr>
<td>Au(α-m-tpdt)₂</td>
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<tr>
<td>Au(α-tb-tpdt)₂</td>
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<tr>
<td>Ni(α-tpdt)₂</td>
</tr>
<tr>
<td>Au(α-tpdt)₂</td>
</tr>
</tbody>
</table>
Ag/AgNO₃ as reference electrode, dichloromethane as solvent, and scan rate 100mV/s. The Fc/Fc⁺ couple was used as internal reference and the values in the table are normalized relatively to it.

- E¹/²⁺ represents dianionic / monoanionic,
- E¹⁺/²⁺ represents monoanionic / neutral,
- E²⁺/³⁺ represents neutral / cationic

**X-Ray Crystallography**

With exception of the neutral compounds 5 and 6, for each ligand and oxidation state, the Ni and Au compounds are isostructural with virtually identical packing pattern. For sake of simplicity only the gold compound is described and details of the nickel analogues can be found in supplementary material. Compound 1 is isostructural to 2 and they crystallize in the monoclinic system, space group C2/c. The asymmetric unit contains half monoanionic complex, [M(α-tbtpd)₂]⁻, and half TPP⁺ cation, with the metal atom at an inversion centre and the P atom at an inversion 2-fold axis. The gold and nickel complexes present the usual square planar coordination geometry, remaining essentially planar with exception of the butyl groups, with angles and bond distances in the usual range of monoanionic dithiothiophenic dithiolates. The thiophenic sulfur atom S3 is found disordered among two positions (S3/S3A, 62/38% and 68/32% for 1 and 2, respectively) corresponding to positional disorder (Figure S3). The TPP⁺ cation also presents the usual geometry (Table S3 and Figure S3/S4).

The crystal structure is composed by chains along c of the [M(α-tbtpd)₂]⁻ anions connected side-by-side by short S3…S3 contacts and S2-H6C-C6 Hydrogen bonds (Fig. 2 and Table S4). The anions of nearby chains are almost perpendicular to each other, making an angle of 80.6°. This arrangement leads to tunnels that are occupied by the TPP⁺ cations connected to the anions by S⁻…H-C hydrogen bonds (Table S4).

Compounds 3 and 4 are isostructural, and crystallize in the triclinic system, space group P-1. The asymmetric unit contains two monoanionic complexes [M(α-bi-isop-tpd)₂]⁻, with the metal at an inversion centre and a TPP⁺ molecule at a general position. The metal complexes in these compounds present a square planar coordination geometry with a slight chair type distortion (Figure S5). Bond distances and angles are identical to those of compounds 1 and 2.

The crystal structure is composed by X-shaped anionic chains, running parallel to a-c. Along the chains, the average molecular plane of the two non-equivalent dithiolate complexes make an angle of 79.2° and the molecules are connected by short S-S contacts (Figure 3, Table S9). TPP⁺ cations occupy the empty space between anions and are connected to them through S⁻…H-C and C-double-bond…H-C hydrogen bonds (Table S9).
Compound 5 crystallizes in the monoclinic system, space group \( P2_1/n \). The unit cell contains one neutral molecule of \([\text{Au}(\alpha\text{-bp-tpdt})_2]\) at a general position. The neutral complex presents the usual square planar coordination geometry (Figure 4 and Figure S7).

A detailed analysis of the bond lengths of the metal bisdithiolene core reveals a significant asymmetry between the two ligands (Table S13) supporting the localization of the unpaired electron in one ligand, as recently found in \([\text{Au}(\text{dm-dddt})_2]\) (dm-dddt = 5,6-dimethyl-5,6-dihydro-1,4-dithiin-2,3-dithiolate).

Besides the slight dihedral angle (11°) due to a folding through S1-S2 atoms, the “oxidized” \( \alpha\text{-tb-tpdt} \) ligand also denotes shorter S_{coord}-C bonds and more regular C-C bonds in the thiophene ring, when compared with the other \( \alpha\text{-tb-tpdt} \) ligand, that stays planar and with bond distances closer to the monoanionic specie in 1. The thiophenic sulfur atoms are found disordered almost equally among two positions: S5/S6A and S6/S6A, with 56/44% and 54/46%, respectively, for 5, and S3/S3A and S6/S6A, with 55/45% and 58/42%, respectively, in the case of 6.

The neutral molecules are associated in pairs related by an inversion center, through two very short S1-S2*, S2-S1* contacts (3.275 Å, *symm. op. 1-x,1-y,-z) connecting ligands with different electronic densities. These pair of molecules are arranged in the crystal structure in chains interacting throughout several side-by-side S_{coord}-S_{coord} short contacts, giving rise to double chains along \( a \). Nearby double chains have molecules tilted in alternated orientation and molecules make an angle of 63.9° (Figure 5).

Compound 6 is not isostructural to 5 although sharing a common molecular packing pattern (Figure 6). The nickel complex has a central core more planar than the gold analogue (Figure 4), without the asymmetry in bond lengths and folding dihedral angle of the related Au complex (Table S15), as expected for a molecule with an even number of electrons. The analysis of the bond lengths in the neutral complex compared with the anionic one reveals that there is mainly a significant shortening of the S_{coord}-C bonds, denoting a ligand centered oxidation process. In 6 the dimers are associated by a long sulfur over metal contacts, at 3.780 Å, rather than ligand-ligand interactions, as in 5 (Figure 4). In the crystal structure the dimers are arranged in layers, connecting with each other by short S2-S2* S3-S3* contacts (3.682 Å, *symm. op. -x,-y,1-z and 3.443 Å, *symm. op. 1-x,-y,-z, respectively). Molecules in different layers are rotate 72° (Figure 6).
Compound 7 is isostructural with 8, crystallizing in the triclinic system, space group P-1. The unit cell contains one neutral complex $[M(\alpha\text{-tb-tpdt})_2]^0$ with the metal atom at an inversion center. These neutral complexes present the usual square planar coordination geometry and with exception of the isopropyl substituents are essentially planar (Figure 4). The bond distances are in the range for other gold and nickel neutral compounds.\textsuperscript{[7][14]} When the neutral complexes of both Au and Ni are compared with the corresponding monoanions it’s clear that the most sensitive bond lengths to the electron removal are the Scoord-C, and the M-S distances are not significantly affected, as previously found in the related methyl substituted complexes.\textsuperscript{[10]}

The crystal structure is composed of regular columns of neutral complexes $[\text{Au}(\alpha\text{-tbtpd})_2]^0$, stacked face-to-face along a (Figure 7). The overlap of the molecules in these stacks involves a displacement essentially along the long axis of the complexes so that the thiophenic sulphur atom of one molecule lies above the metal atom of the next one (Figure 4). This type of overlap with unusually long displacement of the molecules is certainly due to the stereochemical constrains imposed by the alkyl substituents. Also as a consequence of the bulky substituents neither the interplanar distance between central bisdithiolene atoms in a stack (3.483 Å for Au and 3.623 Å for Ni) nor the shorter contacts between molecules in neighboring columns ($d_{S2-S3}=3.748$ Å and $d_{S3-S3}=3.926$ Å, in the case of 7 and $d_{S2-S3}=3.725$ Å and $d_{S3-S3}=3.883$ Å, in the case of 8 ) are below the sum of the van der Waals radii.

An interesting question is raised about the origin of the ligand asymmetry observed in 5 while 7 remains symmetric. Recently it has been suggested that,\textsuperscript{[16]} this is governed not only by the balance between the electronic coupling between the two ligands, H, and the so called Marcus reorganisation energy $\lambda$, but also by intermolecular interactions in the solid state. In this case in view of the similarity of the isopropyl and ter-butyl substituted ligands the first parameters are expected to be essentially the same. Therefore the observed differences should be ascribed to the role of the intermolecular interactions in the solid, providing a clear illustration of the predicted stabilization of the symmetrical configuration by SOMO–SOMO interactions in case of the formation of regular stacks,\textsuperscript{[15]} as in the isopropyl substituted complex 7, while the terbuthyl substituents in 5 do
not allow a regular stacking with good intermolecular interaction and therefore the stable configuration is asymmetric.

Figure 7. Crystal structure of 7 a) viewed along a ; b) partial view showing two neighbouring stacks, viewed along the molecular longest axis.

Electrical Transport Properties

The electrical conductivity, measured in single crystals, at room temperature for 5-8 is rather small, ranging from 10⁻⁵ to 5x10⁻⁵ S/cm. These low values typical of insulators, can be understood as a consequence of the relatively large HOMO-LUMO gap of these complexes preventing any overlap of the corresponding bands in solid state. The neutral gold complexes present one electron in the HOMO which in the solid state, leading in most cases to a half filled band behaving as Mott insulating system. This is confirmed by an analysis of the solid state intermolecular interactions calculated for compounds 5 and 7 using the extended Hückel approximation and a double-ξ basis set. In both cases three type of different possible interactions were considered between molecules along the chains and between nearby chains as indicated in figures 6 and 7. In the case of 5, the calculations show that the strongest interaction (I) is between pair of molecules, overlapped face-to-face, one order of magnitude higher than the interactions (II and III) between molecules placed side-by-side along the chains. In compound 7, the strongest Interactions occurs between molecules stacked in the same column(I) with much smaller interactions between molecules in neighboring stacks (II and III as shown in fig. 7).

Magnetic Properties

The monoanionic Ni and the neutral Au complexes with an odd number of electrons are expected to be paramagnetic while the monoanionic Au and neutral Ni complexes are expected to be diamagnetic. The paramagnetic susceptibility $\chi_P$ of compounds was obtained in the range 2-300 K from measurements with a SQUID magnetometer after a correction for diamagnetism estimated from tabulated Pascal constants. As shown in Figure 8 the paramagnetic nickel compounds 2 and 4 present at room temperature values of $\chi_P T$ product of 0.41 and 0.38 emuK/mol, corresponding to effective magnetic moments of 1.79 $\mu_B$ and 1.74 $\mu_B$, respectively, close to the expected value of 1.73 $\mu_B$ for a $S = \frac{1}{2}$ systems with $g=2$.

$\chi_P T$ of 2 is almost temperature independent from room temperature until circa 30 K with a small increase below this temperature to reach 0.43 emuK/mol. A small but more significant and gradual increase of $\chi_P T$ is observed upon cooling in compound 4 with reaching at 20K a maximum comparable to 2 followed by a decrease to 0.41 emuK/mol at 15.5 K. This increase of $\chi_P T$ upon cooling denotes the presence of dominant ferromagnetic Interactions probably mediated by short S₃–S₆ contacts while in 2 the anions are more isolated.

The neutral gold complex in compound 5 was found to be essentially diamagnetic with a weak paramagnetic contribution corresponding to less than 4 % of $S=1/2$ which is in agreement with a strong antiferromagnetic interaction due to the structural dimerization of the complexes as described above.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Interaction</th>
<th>$S_{ij}10^{-3}$</th>
<th>$H_i$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>I</td>
<td>20.3</td>
<td>487.2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>2.4</td>
<td>56.8</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0.8</td>
<td>18.1</td>
</tr>
<tr>
<td>7</td>
<td>I</td>
<td>13.5</td>
<td>286.8</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.5</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>0.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2: Intermolecular energy interactions $H_{ij}$ (meV) and orbital overlaps, $S_{ij}$ between neutral molecules in compounds 5 and 7 estimated by extended Hückel calculations using a double-ξ approximation.

[17,18,19,20]
The paramagnetic gold compound 7 that presents the neutral complexes in regular stacks shows a significant paramagnetic susceptibility. As shown in Figure 8 (above), upon cooling there is a broad maximum in the paramagnetic susceptibility around 200 K, followed by a decrease upon cooling until ~50 K where it reaches a minimum. At lower temperatures, there is an increase of susceptibility ascribed to a dominating Curie-like tail corresponding to approximately 4.8% S=1/2 spins. By subtracting the Curie contribution the resulting magnetic susceptibility curve, \( \chi - \chi_{\text{Curie}} \) (inset of Figure 8) shows a peak occurring at ~25 K (Figure SI5). The full characterization of this transition requires however additional measurements in single crystals which could not be performed at present stage.

The paramagnetic nature of the nickel compounds 2 and 4 is confirmed by their e.p.r. spectra. In frozen solutions at 77 K spectra consist in a single line 50 G and 20 G wide centered at \( g=2.0425 \) and 2.0485 respectively. The e.p.r. spectra of a polycrystalline sample show a signal typical of rhombic system, characteristic of monoanionic nickel bisdithiolene complexes with \( g_1, g_2 \) and \( g_3 \) values of 2.0887, 2.032 and 2.024, for 2 and 2.0915, 2.0521 and 2.0340 for 4. The neutral gold complexes in 5 and 7 were found to be e.p.r. silent in the solid state. However in dichloromethane solution they showed a single line 25 G wide centered at \( g=2.0019 \) and 2.010 respectively.

Conclusions

In this paper the synthetic route to prepare the first members of two new families of complexes based on ter-buthyl and disopropyl substituted thiophedithiolate ligand, \([M(\alpha-tb-tptd)]^x \) and \([M(\alpha-dp-tptd)]^x \), \( M=Au, Ni \) and \( x=-1 \) and 0 was established. As expected, the effect of appending alkyl groups to the thiophene ring renders the new complexes more soluble in common organic solvents and easier to be oxidized to a stable neutral specie than the related non substituted complexes. In the case of the gold complexes, even the cationic species becomes accessible at relatively low potentials. But this gain in solubility and easier access to differently oxidized species is associated with a loss of the electrical conductivity. This loss of conductivity is a consequence of an inefficient molecular overlapping in solid state due to stereochemical effects of the bulky alkyl substituents.

The crystal structure data of the neutral gold complexes, 5 and 7, both with an odd number of electrons and similar peripheral alkyl groups, provide a clear illustration of the role of the intermolecular interactions in the stabilization of SOMO–SOMO interactions. The small difference between the alkyl substituents is enough to allow a more significant intermolecular interaction in

Indeed the results in the 50-300 K range can be fitted to a Bonner-Fisher model using the following equation valid for \( 2kT/J<0.5 \),

\[
\chi = \frac{(C/T)((0.25+0.149445(J/2kT)+0.30094(J/2kT)^2)/(1+1.9862(J/2kT)+0.68854(J/2kT)^2+6.0626(J/2kT)^3)))}{kT^3/2J}\]

with an antiferromagnetic interaction \( J/2K = -115.5 \) K (solid line ). In the lower temperature region \( (T < 40 \) K) the paramagnetic susceptibility shows a plateau, and then below 25 K a faster decrease towards zero, suggesting an AF transition which may occur as a consequence of additional interchain AF interactions. In fact considering the interactions previously mentioned between stacks, the system is expected to be not strictly one dimensional at low temperatures, but instead behave as an anisotropic two dimensional system, allowing the occurrence of a transition. This possibility of an AF transition was confirmed by AC susceptibility measurements at different frequencies showing the absence of signal in the out-of-phase component, \( \chi'' \), in contrast to the in-phase component, \( \chi' \) that shows a peak occurring at ~25 K (Figure SI5). The full characterization of this transition requires however additional measurements in single crystals which could not be performed at present stage.
5 than in 7, resulting in a stable asymmetric configuration, with the unpaired electron centered in one of the ligands. In compound 7, the dimerization of the complexes is prevented, leading to a regular stacking of paramagnetic complexes with a symmetrical configuration. The paramagnetic [Au(q-dp-tptd)] units present strong antiferromagnetic interactions undergoing an AFM transition at ca. 25 K.

Experimental Section

General experimental conditions: All manipulations were carried out under strict anaerobic conditions under dry nitrogen, unless otherwise stated. All solvents were purified following standard procedures. Other chemicals were commercially obtained and used without any further purification. Compound II, was prepared following a previously reported procedure. Purification. Compound III was added to a solution of 120mg (2 mmol) sodium methoxide in methanol (5mL) and stirred for 30-40min. 45.99mg (0.2 mmol) nickel chloride hexahydrate was dissolved in methanol (1mL) and added to the reaction mixture. The dark red solution obtained is stirred at room temperature for 15 min. A solution of 162.29mg (0.4 mmol) tetracyanophosphonium bromide in methanol (1mL) is then added to the previous reaction mixture, without stirring. No precipitate is formed, the mixture is kept in the glovebox for additional 2 hours and then removed and allowed to oxidize with atmospheric oxygen. Green crystals are formed immediately, the mixture is kept in the fridge overnight and then the crystals are filtered and washed with cold methanol, to afford 118 mg (31%) of brown needles. Elemental analysis calcd (%) for CuH24Au2P2Sc: C 53.00, H 4.85, S 19.29; found C 52.58, H 4.71, S 18.51.

Synthesis of TPP[Ni(α-(bptpdt))], (4): In the glovebox, 100mg (0.4 mmol) ligand III was added to a solution of 120mg (2 mmol) sodium methoxide in methanol (5mL) and stirred for 30-40min. The reaction mixture was formed and the mixture is kept in the glovebox for additional 2 hours. The precipitate dissolves and the mixture is removed from the glovebox and allowed to oxidize with atmospheric oxygen. Brown crystals are formed immediately, the mixture is kept in the fridge overnight and then the crystals are filtered and washed with cold methanol, to afford 118 mg (31%) of brown needles. Elemental analysis calcd (%) for CuH24Au2P2Sc: C 53.00, H 4.85, S 19.29; found C 52.58, H 4.71, S 18.51.

Synthesis of TPP[Ni(α-(bptpdt))], (5): A solution of 13.8 (0.05 mmol) mg iodide in 2mL dichloromethane is slowly added to a solution containing 50 mg (0.05 mmol) of 1 in 4 mL dichloromethane. A dark precipitate is formed immediately, which is centrifuged and washed several times with cold dichloromethane, yielding 15.77 mg of dark brown needles (49%). Elemental analysis calcd (%) for C15H34AuNiS6: C 61.53, H 5.63, S 22.40; found C 61.64, H 5.67, S 21.99.

Synthesis of [Au(α-(dp-tptd))] (6): A solution of 16.1 mg (0.06 mmol) iodide in 2mL dichloromethane is slowly added to a solution containing 50 mg (0.06 mmol) of 2 in 4 mL dichloromethane. A very thin precipitate is formed, which is centrifuged and washed several times with cold dichloromethane, yielding 11.47 mg of green needles (40%). Elemental analysis calcd (%) for C15H34AuNiS6: C 61.47, H 4.35, S 41.51; found C 61.68, H 4.23, S 41.44.

Synthesis of [Au(α-(dp-tptd))] (7): The neutral complex was obtained by slow diffusion in a test tube. A first layer of 10mg (0.01 mmol) of 3 in 10 mL dichloromethane was added to the tube; the interface was formed by 5 mL acetonitrile; the upper layer contains 2.8 mg (0.01 mmol) iodide in 2mL acetonitrile. The product starts precipitating in the interface after 2 hours and is left in the dark overnight. The brown needles are collected by filtration and wash with ether, to yield 3.61mg (55%) of 7. Elemental analysis calcd (%) for C15H34AuNiS6: C 61.52, H 4.29, S 37.03; found C 38.56, H 4.47, S 27.08.

Synthesis of [Ni(α-(bptpdt))] (8): The neutral complex was obtained by slow diffusion in a test tube. A first layer of 8.5mgm ore (0.01 mmol) of 4 in 10 mL dichloromethane was added to the tube; the interface was formed by 5 mL acetonitrile; the upper layer contains 2.54mg (0.01 mmol) iodide in 2mL acetonitrile. The product starts precipitating in the interface after 2 hours and is left in the dark overnight. The green needles are collected by filtration and wash with ether, to yield 4.2mg (81%) of 8. Elemental analysis calcd (%) for C15H34AuNiS6: C 61.52, H 4.29, S 37.03; found C 38.56, H 4.47, S 27.08.

Cyclic voltammetry data were obtained using a BAS C3 Cell Stand. The voltammograms were obtained at room temperature, with scan rate 100 mV/s, Pt wire working and counter electrodes and a Ag|AgNO3 reference electrode (10⁻³ M). The studies were performed in...
dichloromethane solutions of compounds 1-4 (10−3 M) using TBPAPF6 (10−1 M) as the supporting. The redox potentials were normalized relatively to the Fe/Fc couple, which was used as internal reference.

X-ray Crystallography. Selected single crystals were mounted on a loop with protective oil and X-ray data was collected on a Bruker APEX II CCD detector diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) and operating in a a and u scans mode. A semi empirical absorption correction was carried out using SADABS.[23] Data collection, cell refinement and data reduction were done with the SMART and SAINT programs.[23] The structures were solved by direct methods using SIR97[26] and refined by full-matrix least-squares methods using the program SHELXL97[27] using the winGX software package. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP 3.[29]

Electrical Transport Properties: Electrical conductivity and thermopower were measured in single crystals in the temperature range of 50−320 K, using a measurement cell attached to the cold stage of a closed cycle helium refrigerator. In the first step, the thermopower was measured by using a slow AC (ca. 10−3 Hz) technique,[30] by attaching two saturated and magnetic field over modulation, were also taken into account. To control the temperature in the range 4−300 K an Oxford ESR-900 cryostat was used.

Magnetic Properties: The magnetic susceptibility of the different compounds was measured with a S700X SQUID magnetometer (Cryogenic Ltd) in the temperature range 2−300 K under applied magnetic fields up to 1 T. All the data were corrected for diamagnetic contributions from the core diamagnetism estimated using Pascal’s constants: χB = -478.9×10−6 emu/mol (2), χC = -483.2×10−6 emu/mol (4), χD = -262.0×10−6 emu/mol (5), χO = -234.0×10−6 emu/mol (6), χP = -301.2×10−6 emu/mol (7), and χN = -301.2×10−6 emu/mol (8). AC susceptibility measurements in 7 were taken using a MagLab 2000 system (Oxford Instruments). The temperature dependence of the real and imaginary components of AC susceptibility, χ’ and χ”, was measured within 1.7 and 50 K using a 5 Oe oscillating field at frequency 3330 Hz under zero and 1000 Oe static fields.

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