

Transition Metal Bisdithiolene Complexes Based on Extended Ligands with Fused Tetrathiafulvalene and Thiophene Moieties: New Single-Component Molecular Metals

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Abstract: The gold and nickel bisdithiolene complexes based on new highly extended ligands incorporating fused tetrathiafulvalene and thiophene moieties (α -tdt = thiophenetetrathiafulvalenedithiolate and dtdt = dihydrothiophenetetrathiafulvalenedithiolate), were prepared and characterised by using cyclic voltammetry, single crystal X-ray diffraction, EPR, magnetic susceptibility and electrical transport measurements. These complexes, initially obtained under anaerobic conditions as diamagnetic gold monoanionic [$n\text{Bu}_4\text{N}$][Au(α -tdt)₂] (**4**), [$n\text{Bu}_4\text{N}$][Au-

(dtdt)₂] (**3**) and nickel dianionic species [$n\text{Bu}_4\text{N}$][Ni(α -tdt)₂] (**8**), [$n\text{Bu}_4\text{N}$][Ni(dtdt)₂] (**7**), can be easily oxidised to the stable neutral state just by air or iodine exposure. The monoanionic complexes crystallise in at least two polymorphs, all of which have good cation and anion segregation in alternated layers, the anion layers making a dense 2D network of short S...S con-

tacts. All of the neutral complexes, obtained as microcrystalline or quasi amorphous fine powder, present relatively large magnetic susceptibilities that correspond to effective magnetic moments in the range 1–3 μ_{B} indicative of high spin states and very high electrical conductivity that in case of the Ni compound can reach $\sigma_{\text{RT}} \approx 250 \text{ Scm}^{-1}$ with a clear metallic behaviour. These compounds are new examples of the still rare single-component molecular metals.

Keywords: aurates • conducting materials • ligands • magnetic properties • nickelates

Introduction

Bis-1,2-dithiolene transition metal complexes have been at the centre of many studies over the last decade owing to a combination of functional properties, vivid redox behaviour, diversity of molecular geometries and magnetic moments and specific intermolecular interactions that confer them an enormous interest in different fields of research such as those of conducting and magnetic materials, dyes, and non-linear optics, amongst others.^[1] The electronically delocalized core of these square planar complexes, comprising the central metal, four sulfur atoms and the C=C units, accounts for a rich electrochemical behaviour that often undergoes more than one reversible redox processes. Depending on both the metal and the ligand, different stable oxidation states are possible in these complexes ranging from dianionic to cationic and including, in some cases, partially oxidised states. Partially oxidised states of these complexes in the solid state have been associated for a long time with highly

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electrical conductivity^[2] and metallic^[3] or even superconducting properties.^[4]

More recently, square planar neutral metal bisdithiolene complexes were found that are capable of presenting high electrical conductivity, leading to a new type of molecular metals based on neutral species, the so-called single-component molecular metals (SCMM). This was the case of $[\text{Au}(\alpha\text{-tpdt})_2]$ ($\alpha\text{-tpdt}$ = 2,3-thiophenedithiolate) characterised as polycrystalline sample with a room temperature electrical conductivity of $\sigma_{\text{RT}} = 7 \text{ Scm}^{-1}$,^[5] and $[\text{Ni}(\text{tmdt})_2]$ (tmdt = trimethylenetetrafulvalene-dithiolate) obtained as single crystals with $\sigma_{\text{RT}} = 400 \text{ Scm}^{-1}$.^[6] Following a route initially explored by Narvor et al.^[7] Kobayahi and co-workers have succeeded recently in preparing several complexes based on dithiolene ligands containing TTF moieties, that often exhibit SCMM behaviour.^[6a]

Aiming at enlarging this type of complexes we decided to explore new extended dithiolene ligands that incorporate not only TTF, but also thiophenic moieties. The extra thiophenic units were expected to enhance the degree of π -delocalization over the ligand extremity, while the presence of the additional thiophenic sulfur atom can favour the side intermolecular interaction at the ligand periphery, as found in other not so extended thiophene type ligands.^[8] The square planar coordination geometry of metal bisdithiolene complexes is favourable towards solid-state π - π interactions. Extended ligands are also expected to make more accessible the different oxidation states.

In this paper we report the first complexes based on the new sulfur rich extended thiophenic-TTF dithiolene ligands, $\alpha\text{-tdt}$ = 2,3-thiophenetetrafulvalenedithiolate and dtdt = dihydro-thiophenetetrafulvalene-dithiolate, with Au and Ni.

Results and Discussion

The syntheses of the gold and nickel complexes **3–12**, were performed following a general common procedure (Scheme 1) under anaerobic conditions.

The thiophene–dithiolate ligands, $\alpha\text{-tdt}$ and dtdt , were obtained in solution from the corresponding protected precursors, **1** and **2** that have been recently reported by us,^[9] by means of hydrolytic cleavage with $n\text{Bu}_4\text{NOH}$ in a methanol/THF solvent. These ligands, without intermediate isolation, were immediately reacted with potassium tetrachloroaurate or nickel chloride, and were precipitated as grey–bluish and brown tetrabutylammonium salts, respectively. Crystallisation in dimethylformamide

(DMF) affords air stable crystals. The final yields are in the range 44 to 75%. Elemental analysis results indicate tetrabutylammonium salts with a 1:1 stoichiometry in the case of gold(III) complexes, as confirmed by the X-ray crystal structure analysis in single crystals. In the case of nickel, in spite of strict anaerobic conditions, the preparation procedure leads to dianionic complexes that always contain variable amounts of the mononionic complex revealed by the elemental analysis that often indicated a variable cation/anion stoichiometry between 2:1 and 1:1. Pure samples of the Ni monanionic complexes are difficult to obtain because, as shown by cyclic voltammetry studies (see below), the oxidation potentials to the monoanionic state are quite close to the oxidation potential to the neutral state. However a single crystal of **10**, in the monoanionic state, suitable for X-ray analysis was obtained by recrystallisation from a solution of **10** and DMF.

The EPR spectra of frozen solutions prepared from the Ni complexes, prepared in the most stringent anaerobic conditions, show a signal typical of the Ni^{III} bisdithiolene complexes in a square planar coordination.^[1d,11a] The presence of this signal confirms that the monanionic complex is easily formed (Figure 1).

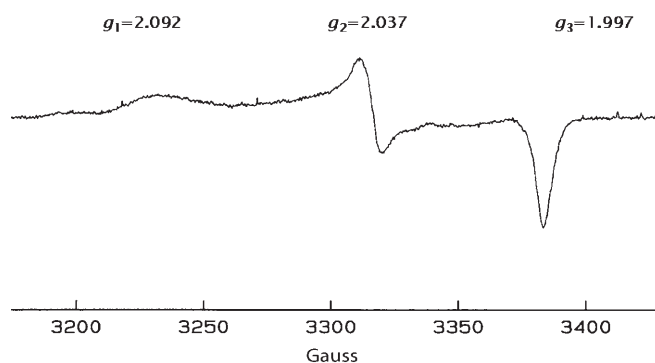
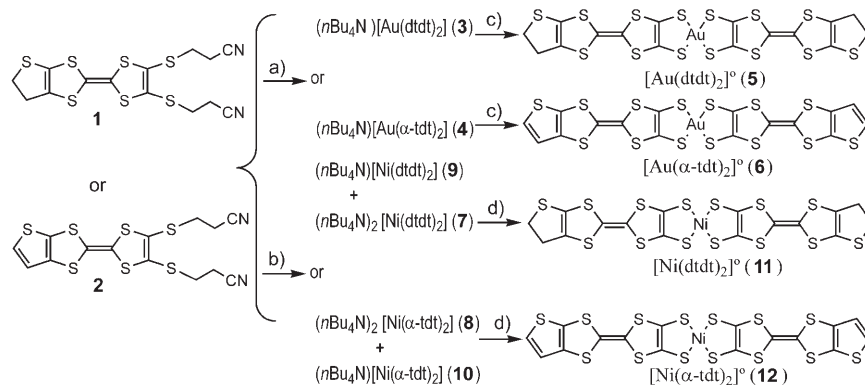


Figure 1. EPR spectrum of $[\text{Ni}(\text{dtdt})_2]^-$ frozen DMF solution, at 77 K.



Scheme 1. Preparation of transition metal complexes **3–12**: a) in THF at -78°C ; $n\text{Bu}_4\text{NOH}$ in MeOH/THF at -78°C ; RT; KAuCl_4 in MeOH/THF at -78°C ; b) in THF at -78°C ; $n\text{Bu}_4\text{NOH}$ in MeOH/THF at -78°C ; RT; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in MeOH/THF at -78°C ; c) I_2 in DMF; d) in DMF by air exposure.

Upon oxidation of the anionic complexes with iodine, or simply by air exposure in the case of the nickel complexes, it was possible to prepare the corresponding neutral Au^{IV} and Ni^{IV} complexes, **5**, **6**, **11** and **12** obtained, in all cases, as an almost insoluble fine dark powder after filtration and thorough washing with dichloromethane. The very low solubility of the neutral complexes in most of the solvents tested, with exception of a slight solubility in thiophene, DMF and DMSO, did not allow, so far, the growth of single crystals suitable for X-ray structure determination. Powder X-ray diffraction studies indicate that these compounds present a variable degree of crystallinity that is correlated with the oxidation procedure. Iodine oxidised samples show an almost completely amorphous behaviour, whereas the Ni samples oxidised by slow air exposure, reveal a microcrystalline behaviour with narrower diffraction lines.

The oxidation behaviour described above for these complexes is consistent with the electrochemical studies.

Cyclic voltammetry of $[n\text{Bu}_4\text{N}][\text{Au}(\alpha\text{-tdt})_2]$ in DMF shows a pair of asymmetric redox waves, centred at -0.715 V versus Ag/AgCl ascribed to the couple $[\text{Au}(\alpha\text{-tdt})_2]^{2-}/[\text{Au}(\alpha\text{-tdt})_2]^-$. At higher potentials there is a pair of quasi-reversible waves centred at $+0.110$ V ascribed to the couple $[\text{Au}(\alpha\text{-tdt})_2]^-/[\text{Au}(\alpha\text{-tdt})_2]^0$. The complex $[n\text{Bu}_4\text{N}][\text{Au}(\text{dtd})_2]$ shows a similar electrochemical behaviour with waves corresponding to the $[\text{Au}(\alpha\text{-dtd})_2]^{2-}/[\text{Au}(\alpha\text{-dtd})_2]^-$ and $[\text{Au}(\alpha\text{-dtd})_2]^-/[\text{Au}(\alpha\text{-dtd})_2]^0$ couples observed, centred at -0.754 V and at $+0.090$ V, respectively. The redox behaviours of the Ni complexes are quite distinct from the Au complexes, but again with no significant differences between the two ligands. For $[n\text{Bu}_4\text{N}][\text{Ni}(\alpha\text{-tdt})_2]$, a pair of quasi-reversible redox waves are observed centred at -0.411 V versus Ag/AgCl ascribed to the couple $[\text{Ni}(\alpha\text{-tdt})_2]^{2-}/[\text{Ni}(\alpha\text{-tdt})_2]^-$, closely followed by a pair of quasi-reversible waves, centred at -0.196 V, that are ascribed to the couple $[\text{Ni}(\alpha\text{-tdt})_2]^-/[\text{Ni}(\alpha\text{-tdt})_2]^0$. The cyclic voltammetry of $[n\text{Bu}_4\text{N}][\text{Ni}(\text{dtd})_2]$ shows also a pair of reversible waves centred at -0.448 V, and a second quasi-reversible wave centred at -0.206 V (-0.141 , -0.272), corresponding to the $[\text{Ni}(\alpha\text{-dtd})_2]^{2-}/[\text{Ni}(\alpha\text{-dtd})_2]^-$ and $[\text{Ni}(\alpha\text{-dtd})_2]^-/[\text{Ni}(\alpha\text{-dtd})_2]^0$ couples, respectively. Such low and closely spaced oxidation potentials in the Ni complexes are consistent with the observed instability of the solutions of $[(n\text{Bu}_4\text{N})_n][\text{M}(\text{dtd})_2]$ that if exposed to air readily give rise to the neutral species, as fine dark precipitates. The higher oxidation potentials of the monoanionic Au complexes are also consistent with the fact that at variance with Ni analogues the air oxidation was found to be irreproducible, and a full oxidation to the neutral state was only reproducibly achieved by using iodine, a stronger oxidant.

Single crystals of **3**, **4** and **10** suitable for X-ray diffraction were obtained from solutions of DMF. The corresponding crystal and structure refining data are listed in Table 1. Two different crystal structures were found both for compound **3** (**3Ph1** and **3Ph2**^[10]) and **4** (**4** and **4-DMF**). The Ni compound **10** is isostructural with its gold analogue **4**. In all cases the metal complexes are in general positions present-

Table 1. Crystal data and structure refinement of compounds **3Ph1**, **4**, **4-DMF** and **10**.

Formula	3Ph1	4	4-DMF	10
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	20.687(3)	9.7170(2)	15.405(2)	9.6252(5)
b [Å]	16.264(2)	9.914(10)	17.268(2)	9.8319(5)
c [Å]	12.417(2)	22.7359(4)	19.002(2)	22.5385(9)
α [°]		91.210(1)	111.165(6)	91.288(3)
β [°]	91.468(9)	101.254(1)	94.702(7)	100.520(2)
γ [°]		109.335(1)	94.638(7)	108.717(3)
V [Å ³]	4176.2(9)	2018.2(4)	4664.6(9)	1978.6(2)
Z	4	4	4	2
R_{int}	0.0719	0.0440	0.0997	0.0662
$R(F^2)$ [$F^2 > \sigma(F^2)$]	0.0334	0.0387	0.063	0.0548
$wR(F^2)$	0.0699	0.0679	0.134	0.1155

ing identical, essentially square planar, coordination geometry (Figure 2) with Ni \cdots S and Au \cdots S bond lengths typical of Ni^{III} and Au^{III}. In the case of compounds **4** and **10**, there is a

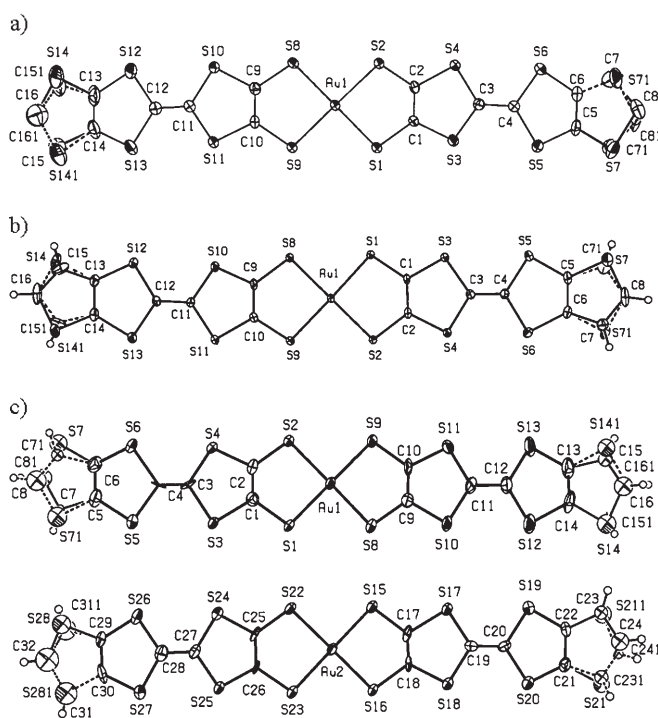


Figure 2. ORTEP views and atomic numbering scheme of a) $[n\text{NBu}_4][\text{Au}(\text{dtd})_2]$, b) $[n\text{NBu}_4][\text{Au}(\alpha\text{-tdt})_2]$ and c) $[n\text{NBu}_4][\text{Au}(\alpha\text{-tdt})_2]\cdot\text{DMF}$ with thermal ellipsoids at 40% probability level.

noticeable tetrahedral distortion (the dihedral angle between the planes defined by the transition metal and the coordination sulfur atoms of each ligand are 11° and 16° , respectively). In these long complexes there are significant non-planar distortions, especially on the terminal thiophenic rings, with respect to the average plane of the complex, which presents a boat type distortion in the case of compound **3** and chair type distortions in the case of compounds **4** and **10**. In the case of compound **4-DMF**, the asymmetric

unit contains two anions, one presenting a chair type distortion and the other a boat type distortion (Figure 3).

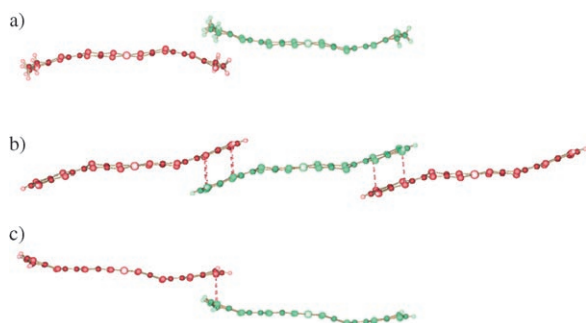


Figure 3. Side view of thiophenic ring contacts between neighbouring anions in the crystal structure of a) **3Ph1**, b) **4** and c) **4-DMF**.

Although not isostructural, all crystal structures present a similar packing pattern with a strong segregation of anions and cations in alternating layers. Anionic and cationic layers are connected through several hydrogen bonds and they alternate along the *b* axis in the case of compounds **3Ph1**, **4-DMF** and **10**, and along the *c* axis in the case of compounds **3Ph2** and **4**. (Figure 4).

In all structures the anionic layers are composed of tightly packed parallel chains of complexes. The complexes are almost parallel to the chain axis and through an overlapping of their terminal thiophenic rings they form domino like chains. Parallel chains are interconnected through several side-by-side short S...S contacts, giving rise to extended 2D networks of contacts (Figure 5). The overlapping modes between anions along one chain differs slightly from structure to structure (Figure 3). In the case of **4** and **10** there is an effective overlapping between anions, through both the thiophenic ring and part of the TTF moiety, with all of the sulfur atoms connected by S...S short contacts. In complexes **3** and **4-DMF**, the overlapping modes between anions is more subtle, involving only the terminal thiophenic ring, with no observed short S...S contacts in case of compound **3**.

In all structures there is severe orientational disorder of the terminal thiophenic sulfur atoms of the α -tdt and dtdt ligands, making it impossible to distinguish between the *cis* and *trans* configurations, as both with orientation disorder could give the observed results. In this respect it is worth referring that other bisdithiolates incorporating thiophenic units were found to crystallise in the *trans* configuration,^[11] and therefore we believe that in the present structures there is orientational disorder of the complexes in the *trans* configuration. Nevertheless, the presence of the *cis* isomer can not be completely ruled out.

As expected for gold(III), with a d^8 configuration in a square planar coordination, the gold monoanionic complexes are diamagnetic. However the oxidised Au^{IV} neutral species are paramagnetic. In the case of nickel compounds it is the reverse. The gold neutral complexes **5** and **6** present as a powder a single EPR line readily visible at room tem-

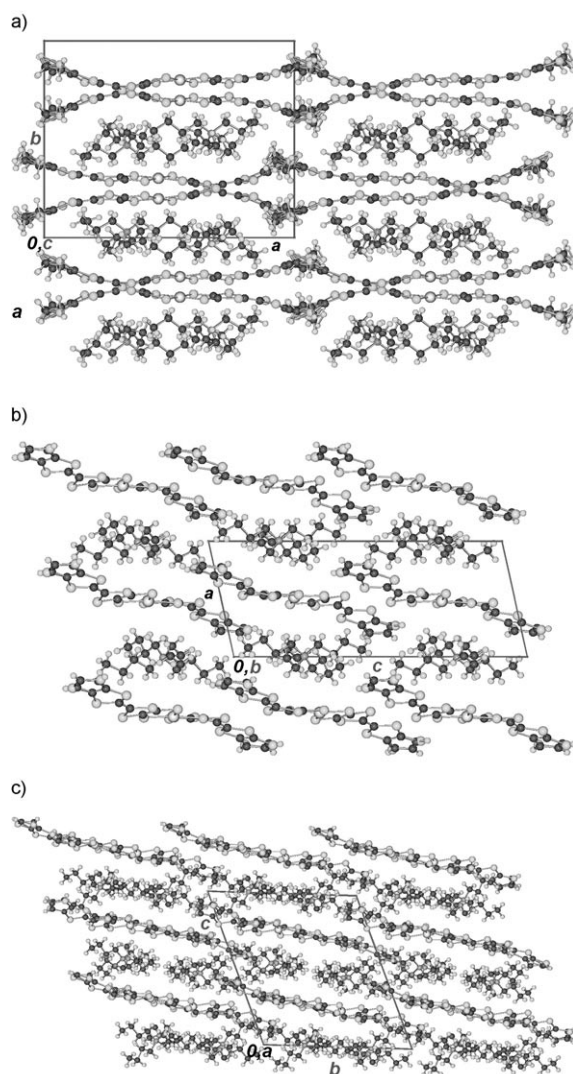


Figure 4. a) View of the crystal structure of **3**, along *c*, b) view of the crystal structure of **4**, along *b* and c) the view of the crystal structure of **4-DMF**, along *a*.

perature, centred at $g=1.94$ and $g=2.0026$ and a line width of 200 and 40 G at 110 K for $[Au(dtdt)_2]$ and $[Au(\alpha\text{-tdt})_2]$, respectively. The shape of these lines shows a strong Dysonian type asymmetry,^[12] typical of highly conducting systems (Figure 6).^[13] For compounds **11** and **12** only a weak EPR signal is observed, comparable to that observed for the dianionic complexes and it is ascribed to the monoanionic complex present as a contaminant.

Static magnetic susceptibility measurements of the neutral compounds in the temperature range 4–300 K show a paramagnetic behaviour. However, at variance with previously reported neutral complexes such as $[Au(\alpha\text{-tpdt})_2]$ ^[5] and $[Ni(\text{tmdt})_2]$ ^[6], which showed a small Pauli like magnetic susceptibility typical of conducting systems, these complexes show rather large values of susceptibility. These large susceptibility values correspond to effective magnetic moments in the range 1–3 μ_B at room temperature, slowly decreasing upon cooling (Figure 7) indicating that these complexes are

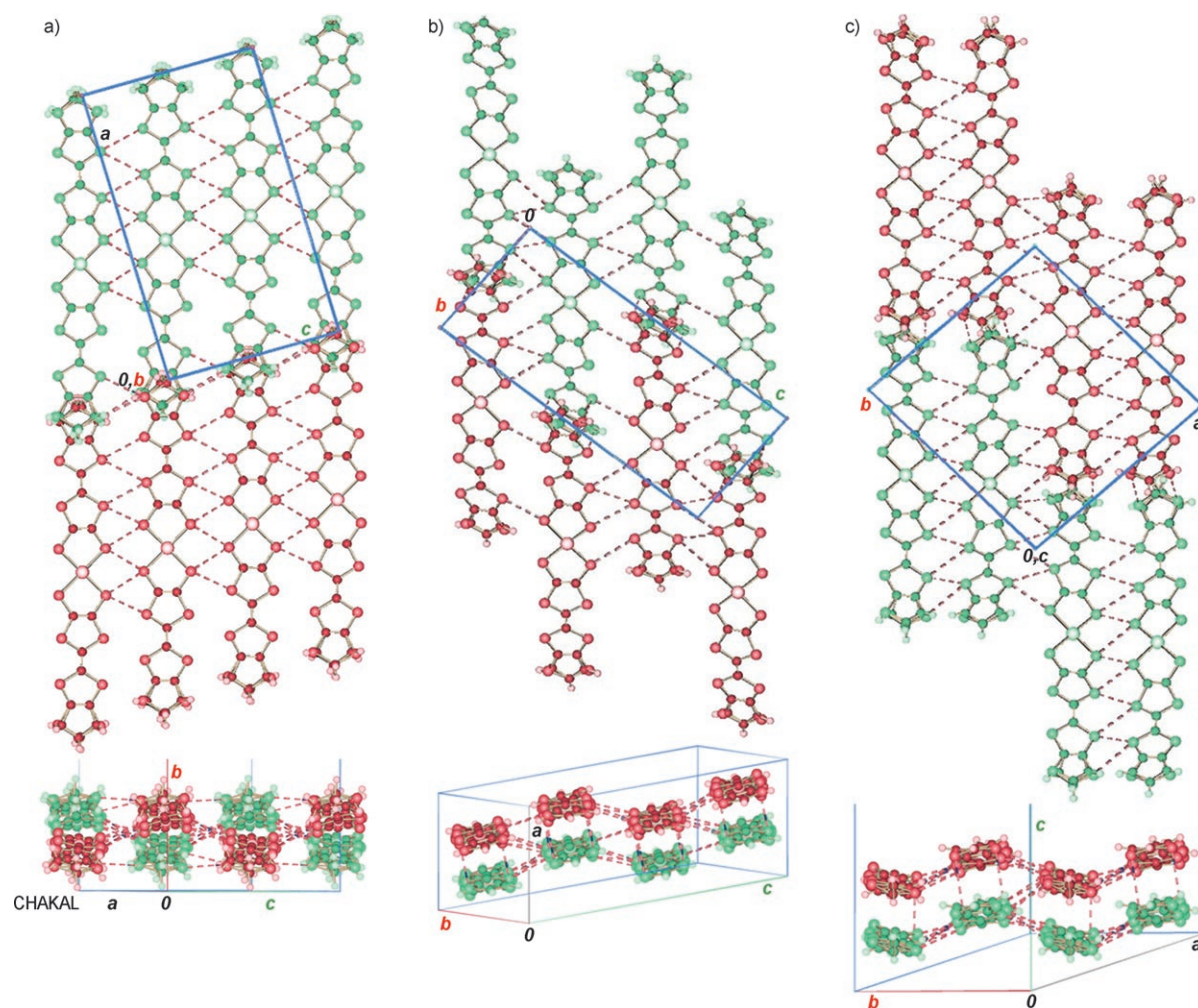


Figure 5. Detail of the crystal structures. The dashed lines represent short S...S contacts. a) One anion layer of **3Ph1** viewed along *b* (top) and along the molecular long axis (bottom). b) One anion layer of **4** viewed along *a* (top) and along the molecular long axis (bottom). c) One anion layer of **4DMF** viewed along *c* (top), and along the molecular long axis (bottom).

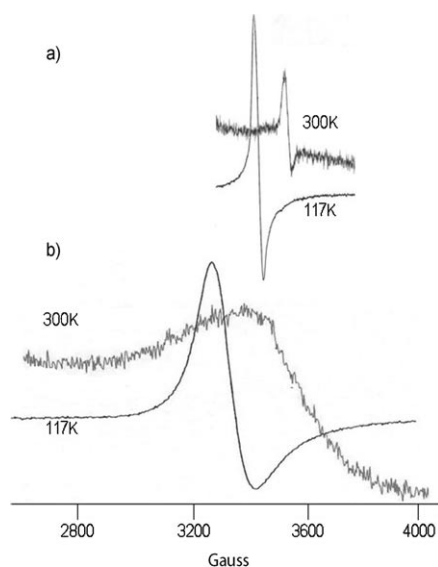


Figure 6. EPR Spectrum of a) $[\text{Au}(\alpha\text{-dtd})_2]$ and b) $[\text{Au}(\text{dtd})_2]$, at 300 K (upper lines) and 117 K (lower lines).

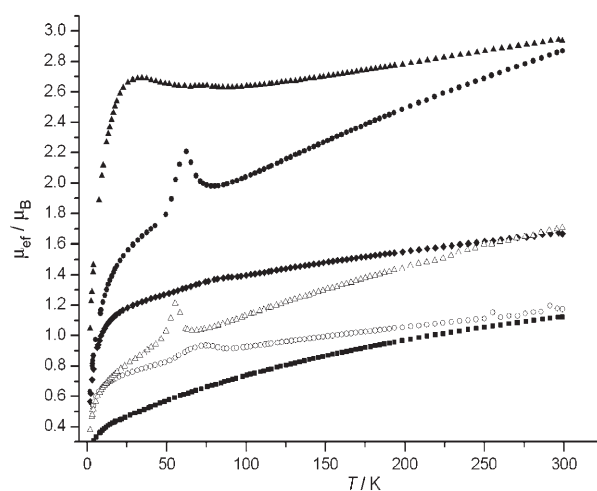


Figure 7. Effective magnetic moment, μ_{eff} of **5** (\blacklozenge), **6** (\blacksquare), **11** (\bullet : oxidation by air exposure, \circ : iodine oxidation) and **12** (\blacktriangle : oxidation by air exposure, \triangle : iodine oxidation) polycrystalline samples as a function of temperature *T*.

in a high spin state, most probably as a consequence of almost degenerated low-lying orbitals. In addition to a Pauli type contribution owing to delocalised electrons in partially filled bands, as expected from the highly conducting properties described below, these compounds have additional unpaired localised electrons responsible for the large susceptibility observed.

The large insolubility of these neutral complexes makes the preparation of crystals large enough for transport measurements very difficult. This prevented any single crystal transport measurements in these compounds that, as mentioned before, tend to be amorphous if prepared by means of iodine oxidation. However four-probe electrical conductivity measurements were performed in compressed powder pellets. These measurements in polycrystalline samples are expected to be dominated by interparticle resistance possibly further enhanced by anisotropy effects. The electrical properties were found to depend also on the oxidation procedure employed to prepare the neutral complexes (Figures 8 and 9). Room temperature electrical conductivity

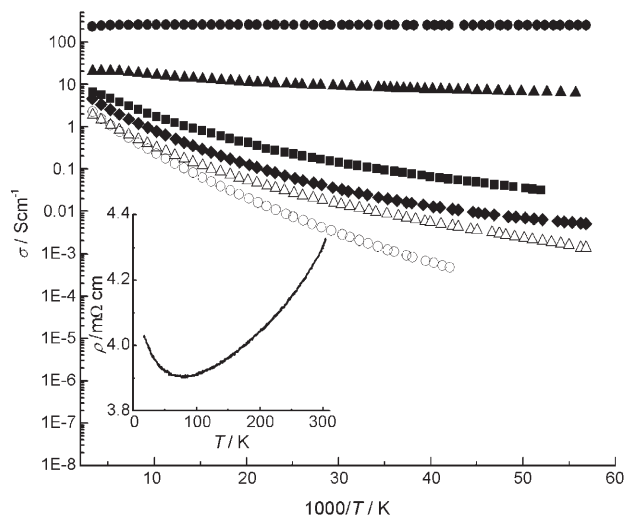


Figure 8. Electrical conductivity, σ , of **5** (\blacklozenge), **6** (\blacksquare), **11** (\bullet): oxidation by air exposure, \circ : iodine oxidation) and **12** (\blacktriangle : oxidation by air exposure, \triangle : iodine oxidation) polycrystalline samples as a function of temperature T . The inset shows the electrical resistivity, ρ , of **11**, obtained by oxidation by air exposure, as a function of temperature, T .

data in these powder samples (Figure 8) indicate values of the order of 2, 2.5, 5 and 8 Scm^{-1} for $[\text{Ni}(\alpha\text{-tdt})_2]$, $[\text{Ni}(\text{dtdt})_2]$, $[\text{Au}(\alpha\text{-tdt})_2]$ and $[\text{Au}(\text{dtdt})_2]$, respectively, obtained by means of iodine oxidation. The more crystalline Ni samples obtained by slow oxidation through air exposure, present higher electrical conductivity values of 200 and 24 Scm^{-1} for $[\text{Ni}(\text{dtdt})_2]$ and $[\text{Ni}(\alpha\text{-tdt})_2]$, respectively. These samples, regardless of their powder nature, are observed at a higher temperature range to display conductivity increasing upon cooling, typical of metals, that extends down to 80 K in case of the highly conducting $[\text{Ni}(\text{dtdt})_2]$ (see inset Figure 8). Notably, taking into account the usual difference between

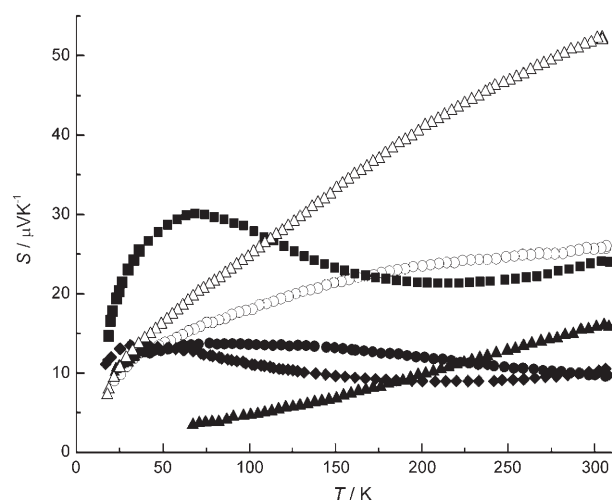


Figure 9. Absolute thermoelectric power of **5** (\blacklozenge), **6** (\blacksquare), **11** (\bullet): oxidation by air exposure, \circ : iodine oxidation) and **12** (\blacktriangle : oxidation by air exposure, \triangle : iodine oxidation) polycrystalline samples as a function of temperature T .

single crystal and powder data, even the samples showing lower conductivity still present exceptionally large conductivity for a compound based on a neutral component. The electrical conductivity activation energy of these compounds is rather small (at most 20 meV at room temperature) and most probably reflects interparticle resistance effects.

The thermopower measurements also show different behaviours dependent on the oxidation procedure (Figure 9). In general the thermopower values are relatively small and compatible with molecular metals. Although, in $[\text{Ni}(\alpha\text{-tdt})_2]$, prepared by air oxidation with a higher crystallinity, is a typical metallic behaviour observed with values decreasing almost linearly with the temperature. It should be considered that thermopower as a zero electrical current measurement, probes the intrinsic properties of the material, and is not so sensitive to the interparticle grain contacts that usually dominate electrical conductivity measurements. The observed temperature dependence of the thermopower is compatible with either very narrow band semiconductors or metals with very small Fermi surfaces.

Finally it should be noted that, in view of the electrical transport properties observed, the magnetic susceptibility of these highly conducting salts is expected to have a Pauli type contribution with values of the order of a $2\text{--}5 \times 10^{-4} \text{ emu mol}^{-1}$, as observed in similar compounds.^[5,6] Remarkably, the large magnetic susceptibilities observed in these compounds are at least one order of magnitude larger, indicating that in addition to delocalised conduction electrons there are unpaired localised electrons. The enlightening of this interesting situation waits for further studies and the possible preparation of single crystals of these neutral complexes.

Conclusions

In conclusion we have prepared Ni and Au complexes of a new family of bisdithiolene complexes based on highly extended ligands incorporating fused tetrathiafulvalene and thiophene moieties. As expected these complexes, initially obtained under anaerobic conditions as diamagnetic Au^{III} and Ni^{II} species, can be readily oxidised to the neutral state by exposure to air or iodine, the intermediate monoanionic Ni^{III} complexes being rather unstable.

The monoanionic complexes crystallise in at least two polymorphic structures, all of them characterised by clear cation and anion segregation in alternated layers, the anion layers presenting a dense 2D network of short S...S contacts. The neutral complexes were obtained as fine powder, quasi-amorphous for iodine oxidation samples and microcrystalline for samples obtained by slow oxidation by air exposure. These neutral complexes are highly conducting and the Ni compounds present, in polycrystalline samples, a clear metallic behaviour of the electrical conductivity, placing them as new examples of single-component molecular metals.

Experimental Section

General Remarks: All manipulations were carried out under strict anaerobic conditions by using a dry nitrogen or argon atmosphere unless otherwise stated. All solvents were purified following standard procedures. 3-[5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4yl)thio] propanenitrile (**1**) and 3-[(5-[(2-cyanoethyl)thio]-2-thieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4yl)thio] propanenitrile (**2**) were synthesised as previously described.¹⁹ Other chemicals were commercially obtained and used without any further purification. Column chromatography was carried out by using silica gel (0.063–0.2 mm). UV-Vis spectra were recorded by using a Cary 5G spectrophotometer (Varian). IR spectra were obtained by using a Perkin-Elmer 577 spectrophotometer. MALDI mass spectra were obtained by using the time-of-flight negative linear mode on an apparatus Kratos Kompact Maldi 2 K probe (KRATOS Analytical) operated with pulsed extraction of the ions. Cyclic voltammetry data were obtained using a BAS C3 Cell Stand. The measurements were performed at room temperature in DMF solutions containing *n*Bu₄NPF₆ as the supporting electrolyte, with a scan rate of 100 mV s⁻¹, platinum wire working- and counter-electrodes and using Ag/AgCl as a reference electrode.

EPR spectra: In the range 4–300 K were obtained by using an X-Band Bruker ESP 300E spectrometer equipped with a microwave bridge ER041XK, a rectangular cavity operating in T102 mode, a Bruker variable temperature unit and an Oxford ESR-900 cryostat and a field controller ER 032M system. The modulation amplitude was kept well below the linewidth and the microwave power well below saturation.

Magnetic susceptibility measurements: In the range 2–300 K were performed by using a longitudinal Faraday system (Oxford Instruments) with a 7 T superconducting magnet, under a magnetic field of 5 T and forward and reverse field gradients of 5 T m⁻¹. Polycrystalline samples (10–15 mg) were placed inside a previously calibrated thin wall Teflon bucket. The force was measured with a microbalance (Sartorius S3D-V). Under these conditions the magnetisation was found to be proportional to the applied magnetic field.

Electrical transport measurements: Electrical conductivity and thermoelectric power measurements of compressed pellets of the polycrystalline material were performed in the range 20–320 K, using a measurement cell attached to the cold stage of a closed cycle helium refrigerator. In a first step thermopower was measured using a slow AC (≈10⁻² Hz) tech-

nique¹⁴ by attaching to the extremities of an elongated sample, with platinum paint (Demetron 308A), two 25 μm diameter 99.99% pure Au wires (Goodfellow Metals) and two 25 μm gold foils thermally anchored to two quartz reservoirs, in a previously described apparatus,¹⁵ controlled by a computer.¹⁶ The oscillating thermal gradient, kept below 1 K, was measured with a differential Au-0.05 at.% Fe versus chromel thermocouple. The sample temperature was measured by a previously calibrated thermocouple of the same type. The absolute thermoelectric power of the sample was obtained after correction for the absolute thermopower of the Au leads, using the data of Huebner.¹⁷ In a second step, the electrical resistivity of the same sample was measured by using a four-probe technique. Two extra Au wires were placed on the sample to achieve a four-in-line contact configuration. Measurements were done imposing through the sample a current of 1 μA at low frequency (77 Hz) and measuring the voltage drop with a lock-in amplifier.

X-ray diffraction experiments: Were performed by means of a Bruker AXS APEX CCD detector diffractometer using graphite monochromated Mo_{Kα} radiation (λ=0.71073 Å), in the φ and ω scans mode. A semi empirical absorption correction was carried out using SADABS.¹⁸ Data collection, cell refinement and data reduction were done with the SMART and SAINT programs.¹⁹ The structures were solved by using direct methods using SIR97²⁰ and refined by using fullmatrix least-squares methods by means of the program SHELXL97²¹ using the winGX software package.²² 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 3.²³ A summary of the crystal data, structure solution and refinement are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 652433, CCDC 652434, CCDC 652435 and CCDC 652436 for compounds [nBu₄N][Au(dtdt)₂] (**3PhI**), [nBu₄N][Ni(α-tdt)₂] (**10**), [nBu₄N][Au(α-tdt)₂]-DMF (**4DMF**) and [nBu₄N][Au(α-tdt)₂] (**4**), respectively. Copies of the data can be obtained free of charge upon application to the director of CCDC, 12 Union Road, Cambridge CB12 1EZ, UK (Fax: (+44)1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Tetrabutylammonium salt of Gold(III) bis-2-(5,6-dihydrothieno[2,3-d]-[1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [nBu₄N][Au(dtdt)₂] (3**):** In a round bottom schlenk, **1** (200 mg, 0.46 mmol) was dissolved in tetrahydrofuran (4 mL), at -78°/-80°C in a nitrogen atmosphere. To this solution was slowly added a 0.1 M solution of tetrabutylammonium hydroxide in methanol (29 mL, 2.0 mmol) over 5 min, while maintaining the temperature at -78°/-80°C. After 10 min the solution was allowed to slowly reach room temperature, after which it was further stirred for 3 h. The solution was then cooled down to -78° and KAuCl₄ (87.6 mg, 0.24 mmol) in methanol (6 mL) was dropwise added under stirring over 5 min. The solution was allowed to slowly reach room temperature remaining in the cooling bath overnight. The solution was filtered, the grey-bluish precipitate was washed with methanol (3 × 10 mL) and diethyl ether (2 × 10 mL) and dried over a vacuum. Crystals suitable for X-ray diffraction measurements were obtained from a slowly cooled DMF solution. Yield=69%; m.p. decomposes at 177°C; ¹H NMR (250 MHz, [D₆]DMSO, TMS): δ=0.935 (t, J=7.95 Hz; 12H), 1.311 (m, J=7.33 Hz; 8H), 1.558 (m, J=7.33 Hz; 8H), 2.831 (t, J=8.0 Hz; 4H), 3.165 (m, J=8.4 Hz; 8H), 3.786 ppm (t, J=8.0; 4H); FTIR (KBr): $\bar{\nu}$ =347 (m, Au-S), 797 (s, C-H aliph), 877 (m, C-H aliph), 1262 (s) (H₂C-CH₂ ligand) 1379 (m) (C-H aliph), 1465 (m) (C H aliph), 2869 (m) (C-H aliph), 2956 cm⁻¹ (m) (C-H aliph); MS: m/z (%): 521 (3) [C₈H₄S₂Au⁻], 489 (7) [C₈H₄S₆Au⁻], 324 (20) [C₈H₄S₇⁻], 325 (17) [C₈H₅S₇⁺], 242 (100) [nBu₄N⁺], 197 (54) [Au⁺]; elemental analysis calcd (%) for C₃₂H₄₄NS₄Au: C 35.31, H 4.07, N 1.29, S 41.24; found: C 36.39, H 4.86, N 1.61, S 37.75.

Tetrabutylammonium salt of Gold(III) bis-2-(thieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [nBu₄N][Au(α-tdt)₂] (4**):** This compound was prepared as a grey-bluish precipitate following the same method as for **3**, using as initial reactive compound **2** instead of **1**. Crystals suitable for X-ray measurements were obtained from slowly cooling DMF solutions. Yield=75%; m.p. decomposes at 206°C; ¹H NMR

(250 MHz, [D₆]DMSO, TMS): δ = 0.935 (t, J = 7.95 Hz; 12H), 1.311 (m, J = 7.33 Hz; 8H), 1.558 (m, J = 7.33 Hz; 8H), 3.165 (m, J = 8.4 Hz; 8H), 7.106 (d, J = 5.4 Hz; 2H), 7.614 ppm (d, J = 5.4 Hz; 2H); FTIR (KBr): $\tilde{\nu}$ = 347 (m) (Au–S), 682 (m) (HC=CH ligand), 797 (s) (C–H aliph), 898 (m) (C–H aliph), 1379 (m) (C–H aliph), 1479 (m) (C–H aliph), 2869 (m) (C–H aliph), 2957 cm⁻¹ (m) (C–H aliph); MS: m/z (%): 519 (5) [C₈H₂S₇Au⁻], 322 (23) [C₈H₂S₇⁻], 290 (100)[C₈H₂S₆⁻], 242 (100) [nBu₄N⁺], 197 (30) [Au⁺]; elemental analysis calcd (%) for AuC₃₂H₄₀NS₁₄: C 35.44, H 3.72, N 1.29, S 41.39; found: C 34.55, H 3.94, N 1.48, S 37.66.

Bistetrabutylammonium salt of Nickel(II) bis-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [(nBu₄N)₂][Ni(dtdt)₂] (7): This compound was prepared following the same procedure as for **3**, using NiCl₂·6H₂O (55.2 mg, 0.23 mmol) instead of KAuCl₄. The product was obtained as a brown powder. Yield = 48%; m.p. decomposes at 163 °C; ¹H NMR (250 MHz, [D₆]DMSO, TMS): δ = 0.935 (t, J = 7.95 Hz; 12H), 1.311 (m, J = 7.33 Hz; 8H), 1.558 (m, J = 7.33 Hz, J = 8.2 Hz; 8H), 2.817 (t, J = 8.2 Hz; 4H), 3.165 (m, J = 8.4 Hz; 8H), 3.773 (t, 4H); FTIR (KBr): $\tilde{\nu}$ = 764 (w) and 883 (m) (CH₂ and CH₃ aliph), 1140 (w) (CH₂ thiophenic ring), 1317 (s) (Ni–S), 1385 (w) and 1458 (m) (thiophenic ring), 2870 (m), 2927 (m) and 2956 cm⁻¹ (m) (C–H aliph); MS: m/z (%): 706 (47) [C₁₆H₈S₁₄Ni⁻], 242 (100) [nBu₄N⁺]; elemental analysis calcd (%) for NiC₄₈H₈₀N₂S₁₄: C 48.33, H 6.76, N 2.35, S 37.64; calcd for NiC₃₂H₄₀NS₁₄: C 40.64, H 4.67, N 1.47, S 47.23; found: C 40.11, H 6.42, N 2.34, S 43.35.

Bistetrabutylammonium salt of Nickel(II) bis-2-(thieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [(nBu₄N)₂][Ni(α-tdt)₂] (8): The compound was prepared following the same procedure as for **7**, but using as initial reactive compound **2** instead of **1**. Crystals suitable for X-ray measurements were obtained from slowly cooling DMF solutions Yield = 44%; m.p. decomposes at 160 °C; ¹H NMR (250 MHz, [D₆]DMSO, TMS): δ = 0.935 (t, J = 7.95 Hz; 12H), 1.311 (m, J = 7.33 Hz; 8H), 1.558 (m, J = 7.33 Hz; 8H), 3.165 (m, J = 8.4 Hz; 8H), 7.011 (d, 2H), 7.617 ppm (d, 2H); FTIR (KBr): $\tilde{\nu}$ = 693 (m) (HC=CH ligand), 797 (s) (C–H aliph), 893 (m) (C–H aliph), 1379 (m) (C–H aliph), 1478 (m) (C–H aliph), 2870 (m) (C–H aliph), 2957 cm⁻¹ (m) (C–H aliph); MS: m/z (%): 702 (43) [C₁₆H₈S₁₄Ni⁻], 242 (100) [nBu₄N⁺]; elemental analysis: calcd (%) for NiC₄₈H₇₆N₂S₁₄: C 48.50, H 6.44, N 2.36, S 37.76; calcd for NiC₃₂H₄₀NS₁₄: C 40.62, H 4.26, N 1.48, S 47.44; found: C 44.36, H 7.13, N 2.23, S 38.01.

Gold(IV) bis-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [Au(α-tdt)₂] (5): Anionic gold complex **3** (40 mg, 0.037 mmol) was dissolved with stirring in a flat bottom flask in dimethyl formamide (2 mL). To this solution it was added iodine (427 mg, 50 mL) in DMF (1.1 mL). After stirring during 24 h, the suspension formed, was centrifuged to separate the solid, was washed with dichloromethane, centrifuged and decanted. The final black powder solid was dried under vacuum. Yield η = 84%; m.p. decomposes at 215 °C; elemental analysis calcd (%) for C₁₆H₈S₁₄Au: C 22.71, H 0.95, N 0.00, S 53.06; found: C 23.95, H 1.04, N 0.62, S 50.56.

Gold(IV) bis-2-(thieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [Au(α-tdt)₂] (6): Using as starting material **4** and following the same procedure used for **5**, the neutral species was obtained as a fine powdered dark solid. Yield η = 82%; m.p. decomposes at 326 °C; elemental analysis calcd (%) for C₁₆H₈S₁₄Au: C 22.82, H 0.48, S 53.31; found: C 22.96, H 0.64, N 0.56, S 47.69.

Nickel(IV) bis-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [Ni(dtdt)₂] (11): Anionic nickel complex **7** (40 mg, 0.034 mmol) was dissolved in dimethyl formamide (2 mL) with stirring in a flat bottom flask. The solution was stirred for 24 h in open air after which it was centrifuged at 3000 rpm for 20 min and decanted. The deposited solid was repeatedly washed with dichloromethane, being centrifuged and decanted each time, and dried under vacuum. Product was obtained as black powder. Yield η = 74%; m.p. decomposes at 225 °C; MS: m/z (%): 706 (40) [M⁻], 706 (52) [M⁺]; elemental analysis calcd (%) for C₁₆H₈S₁₄Ni: C 27.15, H 1.14, S 63.42; found: C 25.70, H 0.96, S 56.90.

Nickel(IV) bis-2-(thieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, [Ni(α-tdt)₂] (12): Using as starting material **8** and following the same procedure used for **11**, the neutral species was obtained as a fine powdered dark solid. Yield η = 50%; m.p. decomposes at 252 °C; MS:

m/z (%): 702 (91) [M⁻], 702 (51) [M⁺]; elemental analysis calcd (%) for C₁₆H₈S₁₄Ni: C 27.30, H 0.57, N 0.00, S 63.78; found: C 26.14, H 0.73, N 0.37, S 58.87.

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