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


Abstract: The gold and nickel bisdithiolene complexes based on new highly extended ligands incorporating fused tetrathiafulvalene and thiophene moieties (a-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 \([nBu_4N][Au(a-tdt)](4)\), \([nBu_4N][Au(dtdt)](3)\) and nickel dianionic species \([nBu_4N][Ni(\alpha-tdt)](8)\), \([nBu_4N][Ni(dtdt)](7)\), 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 contacts. 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 \(\mu_B\) indicative of high spin states and very high electrical conductivity that in case of the Ni compound can reach \(\sigma_{RT} \approx 250 \text{S cm}^{-1}\) 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 nonlinear 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 [Au(α-tptdt)] (α-tptdt = 2,3-thiophenedithiolate) characterised as polycrystalline sample with a room temperature electrical conductivity of \( \sigma_{RT} = 7 \text{ S cm}^{-1} \)[5] and [Ni(tmdt)] (tmdt = trimethylene tetrafluoridaphenyl methanol) obtained as single crystals with \( \sigma_{RT} = 400 \text{ S cm}^{-1} \).[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.[8]

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-de-localization 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 thiophenic type ligands.[9] 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, α-ttdt = 2,3-thiophenetetrafluoridaphenyl methanol and dtdt = dihydro-thiophenetetrafluoridaphenyl methanol, 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, α-ttdt 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 \( \text{nBu}_2\text{NOH} \) 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 mononionic complexes are difficult to obtain because, as shown by cyclic voltammetry studies (see below), the oxidation potentials to the mononionic state are quite close to the oxidation potential to the neutral state. However a single crystal of 10, in the mononionic 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[5] bisdithiolene complexes in a square planar coordination.[1,11] The presence of this signal confirms that the mononionic complex is easily formed (Figure 1).

![Figure 1. EPR spectrum of [Ni(dtdt)_2]^+] frozen DMF solution, at 77 K.](image)

Scheme 1. Preparation of transition metal complexes 3–12: a) in THF at –78°C; \( \text{nBu}_2\text{NOH} \) in MeOH/THF at –78°C; RT; KAuCl\(_4\) in MeOH/THF at –78°C; b) in THF at –78°C; \( \text{nBu}_2\text{NOH} \) in MeOH/THF at –78°C; RT; NiCl\(_2\)-6H\(_2\)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 AuIV and NiII 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 complexes, respectively. Such low and closely spaced oxidation potentials in the Ni complexes are consistent with the observed instability of the solutions of the Ni complexes, 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 (3PhI and 3PhII) and 4 (4 and 4-DMF). The Ni compound 10 is isomorphous with its gold analogue 4. In all cases the metal complexes are in general positions presenting identical, essentially square planar, coordination geometries (Figure 2) with Ni−S and Au−S bond lengths typical of NiII and AuIII. In the case of compounds 4 and 10, there is a 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 thiophene 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).

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 \( 3\text{Ph1} \), \( 4\text{-DMF} \) and \( 10 \), and along the \( c \) axis in the case of compounds \( 3\text{Ph2} \) 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 \( 4\text{-DMF} \), 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 \( \alpha\text{-tdt} \) and \( \text{dttd} \) 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(I), 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 temperature, centred at \( g=1.94 \) and \( g=2.0026 \) and a line width of 200 and 40 G at 110 K for \([\text{Au(dttd)}]_2\) and \([\text{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 di-anionic 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 \([\text{Au(\(\alpha\text{-tpdt})]}_2\)]\(^{10}\) and \([\text{Ni(\(\text{tmdt})]}_2\)]\(^{11}\), 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 \( \mu_B \) 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 4·DMF viewed along c (top), and along the molecular long axis (bottom).

Figure 6. EPR Spectrum of a) [Au(α-tdt)₂] and b) [Au(dtdt)₂], at 300 K (upper lines) and 117 K (lower lines).

Figure 7. Effective magnetic moment, $\mu_{ef}$, of 5 (○), 6 (●), 11 (●: oxidation by air exposure, ★: iodine oxidation) and 12 (△: oxidation by air exposure, ◆: 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 of iodine oxidation. The more crystalline Ni samples, obtained by slow oxidation through air exposure, prepare 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 2–5 \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.

![Figure 8. Electrical conductivity, $\sigma$, of 5 (●), 6 (●), 11 (●) oxidation by air exposure, 6 iodine oxidation and 12(●) oxidation by air exposure, 6 iodine oxidation polycrystalline samples as a function of temperature $T$. The inset shows the electrical resistivity, $\rho$, of 11, obtained by oxidation by air exposure, as a function of temperature, $T$.](image)

![Figure 9. Absolute thermoelectric power of 5 (●), 6 (●) 11 (●) oxidation by air exposure, 6 iodine oxidation and 12(●) oxidation by air exposure, 6 iodine oxidation polycrystalline samples as a function of temperature $T$.](image)
Conclusions

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

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-[[2-cyanoethylthio]-2-(5,6-dihydrothieno[2,3-d]-1,3]dithiol-2-yldiene-1,3-dithiol-4-y]thio propanenitrile (I) and 3-[[2-cyanoethylthio]-2-thieno[2,3-d]-1,3]dithiol-2-yldiene-1,3-dithiol-4-y]thio propanenitrile (2) were synthesised as previously described. Other chemicals were commercially obtained and used without any further purification. Column chromatography was carried out using silica gel (0.063–0.2 mm). UV-Vis spectra were recorded using a Cary 50 spectrophotometer (Varian). IR spectra were obtained using a Perkin-Elmer 577 spectrophotometer. MALDI mass spectra were obtained 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 nBu\textsubscript{4}NP\textsubscript{F} as the supporting electrolyte, with a scan rate of 100 mV s\textsuperscript{-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 T02 mode, a Bruker variable temperature unit and an Oxford ESR-900 cryostat and a field controller ER 032 m 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 for temperatures between 2 and 300 K. The magnetic moment was obtained using the double-derivative magnetic AC susceptibility method.

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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\textsuperscript{-3} Hz) technique by attaching to the extremities of an elongated sample, with platinum paint (Demetron 308A), two 25 μm diameter 99.999% pure Au wires (Goodfellow Metals) and two 25 μm gold foils thermally anchored to two quartz reservoirs, in a previously described apparatus, controlled by a computer. The temperature gradient, kept below 1 °C, 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. 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 ω scan mode. A semi empirical absorption correction was carried out using SADABS. Data cell refinement and data collection were performed using SMART and SAINT programs. The structures were solved by using direct methods using SIR92 and refined by using full-matrix least-squares methods by means of the program SHELXL97. EPR spectra were obtained using a Bruker ESP 300E spectrometer equipped with a microwave bridge ER041XK, a rectangular cavity operating in T02 mode, a Bruker variable temperature unit and an Oxford ESR-900 cryostat and a field controller ER 032 m system. The magnetic moment was obtained using the double-derivative magnetic AC susceptibility method.

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(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): v = 1637 cm⁻¹ (m) (Au–S), 2877 (m) (HC–CH ligand), 2975 cm⁻¹ (m) (C–H aliph), 3068 cm⁻¹ (m) (C–H aliph), 3095 cm⁻¹ (m) (C–H aliph), 2957 cm⁻¹ (m) (C–H aliph); MS: m/z (%): 519 (5) [C₂H₉Au⁺], 322 (23) [C₈H₆S₄⁺], 290 (100) [C₄H₆S₂⁺], 242 (100) [Bu₄N⁺]; elemental analysis calculated (%) for AuC₄H₆S₄Ni: C 34.57, H 3.47, N 1.31, S 58.67.

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[10] Due to unsolved ligand disorder in the structure, only the cell pa- rameters were obtained for 3Ph₂: Monoclinic, P2₁/n, a = 9.885(5), b = 2.584(5), c = 16.510(5) Å, β = 95.05(5)°.


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