



Review

Transition metal complexes based on thiophene-dithiolene ligands

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Contents

1. Introduction	1480
2. Complexes based on simple conjugated fused thiophene-dithiolate ligands	1481
2.1. Synthesis and redox behaviour	1481
2.2. Crystal and molecular structures	1483
2.3. Magnetic properties	1484
2.4. Electrical transport properties	1485
3. Complexes based on extended dithiophene ligands	1486
3.1. Synthesis and redox behaviour	1487
3.2. Crystal structures	1487
3.3. Electronic transport properties	1488
3.4. Magnetic properties	1490
4. Polymerisable thiophene-functionalised metal dithiolenes	1490
5. Conclusions	1491
Acknowledgements	1491
References	1491

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ABSTRACT

The chemistry of transition metal dithiolene complexes based on thiophene-dithiolene ligands (TD) is reviewed, from the ligand synthesis and complex preparation to the molecular structure and solid state physical properties of different compounds based on them. The ligands considered are based mainly either on simple thiophene-dithiolenes (α -tpdt = 2,3-thiophenedithiolate, dtptd = 4,5-dihydro-2,3-thiophenedithiolate, and tpdt = 3,4-thiophenedithiolate), or in more extended and delocalised dithiolate ligands (α -tdt = 3-({5-[(2-cyanoethyl)thio]-2-thieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile and dttd = 3-({5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile) that besides the thiophenic ring also incorporates a fused TTF moiety. Dithiolene complexes based on ligands containing appended thiophenic units will also be briefly considered. The structural variability of these complexes that in addition to the usual square planar coordination geometry, $M(TD)_2$, can also present dimeric, $[M(TD)_2]_2$, or cluster structures such as $[Cu_4(TD)_3]$ and $[Ni_4(TD)_6]$, is addressed. The role of the thiophene group and its ability to enhance electronic delocalisation from the metal dithiolene core throughout the ligand and to establish solid state networks of S...S interactions is discussed. The importance of these complexes as useful building blocks to prepare molecular materials with very interesting magnetic and transport properties, ranging from metamagnets to Single Component Molecular Metals, is illustrated by different compounds based on them.

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Abbreviations: PT, polythiophene; ttpdt, 5-(2-thienyl)-2,3-thiophenedithiolate; tedt, 1,2-di(2-thienyl)-1,2-ethenedithiolate; tertdt, terthiophenedithiolate; mtertdt, methylterthiophenedithiolate; mpdt, 2,5-bis(para-methoxyphenyl)thiophenedithiolate; α -tpdt, 2,3-thiophenedithiolate; tpdt, 3,4-thiophenedithiolate; dtptd, 2,3-dihydro-5,6-thiophenedithiolate; TTF, tetrathiofulvalene; BET-TTF, bis(ethylenethio)tetrathiofulvalene; DT-TTF, dithiophene-tetrathiofulvalene; α -DT-TTF α , -dithiophene-tetrathiofulvalene; α -tdt, 3-({5-[(2-cyanoethyl)thio]-2-thieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile; dttd, 3-({5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile); tdt, 3-({5-[(2-cyanoethyl)thio]-2-thieno[3,4-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile; mnt, maleonitriledithiolate; dcdbt, 4,5-dicyanobenzene-1,2-dithiolate; dmit, 4,5-dimercapto-1,3-dithiole-2-dithione; bdt, benzodithiolate; SCMM, single component molecular metal; SCO, spin-crossover; TD, thiophene-dithiolene; tmdt, trimethylenetetrathiofulvalenedithiolate; $M(Cp^*)$, decamethylmetalocenium; HCl-5-qsal, N-(8-quinolyl)-5-chlorosalicylaldehyde; BzPy, benzylpyridinium.

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1. Introduction

Bis-1,2-dithiolene transition metal complexes have been extensively studied for almost four decades due to their combination of functional properties, vivid redox behaviour, diversity of molecular geometries, magnetic moments and specific intermolecular interactions. This has led to great interest in different fields of research such as those of conducting and magnetic materials, non-linear optics, catalysis and bioinorganic chemistry among others [1]. The electronically delocalised core comprising the central metal, four sulphur atoms and the C=C units, accounts for a rich electrochemical behaviour that often yields one or more reversible redox processes. The redox properties of these complexes are strongly dependent on the ligand and its, generally large, contribution to the frontier orbitals. The possible oxidation states of these complexes range from dianionic to cationic states and partial oxidation situations often occurring especially in the solid state. Also different spin states such as $S=0$, $1/2$, 1 or $3/2$, can be easily obtained, upon variation of both the transition metal M and oxidation state making these complexes also suitable units for magnetic materials. Furthermore these complexes also show a diversity of geometry, ranging from the more general case of purely square planar coordination, favourable to solid state extended π - π interactions, to dimeric, trimeric [2] or even polymeric [3] arrangements. All these features have made dithiolene complexes suitable building blocks for the preparation of electrical and magnetic materials

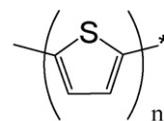
The so called innocent or non-innocent role of the ligands in the properties of these complexes and their ability to stabilise the different oxidation states has been subject of continued debate until present [4]. Despite this controversy it is clear that both the accessibility to a wider range of oxidation states and the larger intermolecular solid state interactions between neighbouring species are enhanced by the more extended ligands contributing to a more delocalised ligand centred HOMO.

It was found early that the occurrence of high electrical conductivity and metallic properties in these complexes is often associated with partially oxidised states, as in the case of the one-dimensional conductor $[\text{Pt}(\text{mnt})_2]\text{Li}_{0.75}\cdot 2\text{H}_2\text{O}$ (mnt = maleonitriledithiolate) [5], one of the first inorganic molecular metals, and of the $\text{TBA}_2[\text{M}(\text{dcbdt})_2]_5$ series (dcbdt = 4,5-dicyanobenzene-1,2-dithiolate, with $M = \text{Au}$, Cu and Ni) [6]. The use of a more extended and sulphur rich ligand, as in $\text{Ni}(\text{dmit})_2$ salts (dmit = 4,5-dimercapto-1,3-dithiole-2-dithione), has made possible the first molecular inorganic superconductors [7].

The applications of the transition metal bisdithiolene complexes as building blocks for conducting and magnetic materials are expected to be strongly favoured by more extended ligands containing heteroatoms such as sulphur, nitrogen or oxygen. While the extended nature of the π -ligands makes the different oxidation states more easily accessible and favours larger solid state π - π interactions, the presence of heteroatoms favours more tridimensional interactions, namely through $\text{S}\cdots\text{S}$ contacts. This review will focus specifically on dithiolene complexes incorporating thiophene moieties in the ligands that in this context have been explored during the last 10 years.

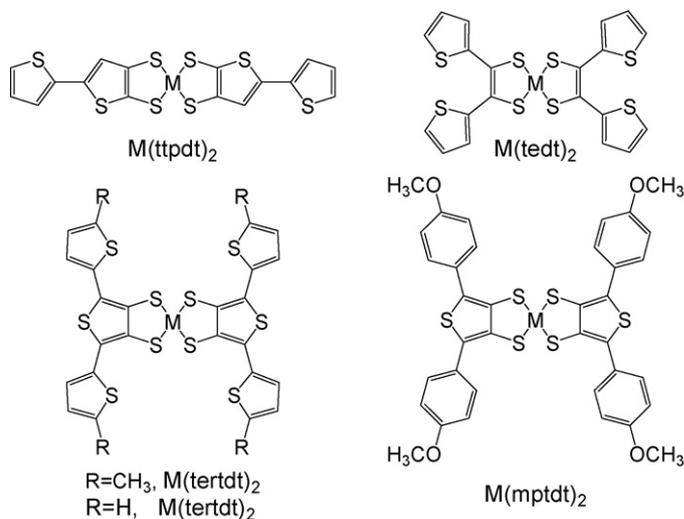
Several electroactive molecular materials containing the thiophene ring were previously reported. Polythiophene, and its derivatives are known for more than 20 years as a family of polymers with peculiar electronic transport properties (p-type semiconductors). In these materials the p-type nature comes from the low ionization potential derived from the extended π -system. Some derivatives have been made as promising easy solution processing materials for field-effect transistors [8] (Scheme 1).

Recently a few examples of transition metal dithiolates, which include in their structure thiophenic rings, regarded as monomers to obtain the corresponding polythiophene polymers



Polythiophene (PT)

Scheme 1. Polythiophene (PT).

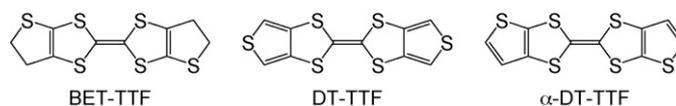


Scheme 2.

by means of electrochemical polymerisation, have been reported. These are in general thiophene rings appended to the dithiolene group without direct or with reduced π -interaction with the C_2S_2 dithiolene core and they include complexes based on the bis(5-(2-thienyl)-2,3-thiophenedithiolate) (tpdt) [9] and on the bis[1,2-di(2-thienyl)-1,2-ethenedithiolate] (tedt) [10] ligands or dithiolene complexes bearing terthiophene (tertdt and mtertdt) and 2,5-bis(para-methoxyphenyl)thiophene (mptdt) units (Scheme 2) [11].

However the characterisation of these complexes has been essentially focused on their electrochemical polymerisation ability. Since this type of dithiolenes with appended thiophenes are included in a specific review in this issue by S. Dalgleish and N. Robertson [12], they will be only very briefly mentioned here in the last section.

Another type of thiophene-dithiolate complexes that have been better characterised as crystalline materials during recent years are based on simple conjugated thiophene-dithiolate ligands such as tpdt = 3,4-thiophenedithiolate, α - tpdt = 2,3-thiophenedithiolate and dtpdt = 2,3-dihydro-5,6-thiophenedithiolate (Scheme 4), where the thiophene group is directly coupled to the sulphur-metal chelating system [13]. The transition metal complexes with tpdt , α - tpdt and dtpdt ligands are the inorganic analogues of the previously known organic TTF type donors BET-TTF (bis(ethylenethio)tetrathiofulvalene), DT-TTF (dithiophene-tetrathiofulvalene) or α -DT-TTF (Scheme 3) [14], where the central C=C double bond is replaced by a transition metal in a MS_4 environment. These organic electronic donors have been at the basis of several molecular materials with interesting electrical



Scheme 3.

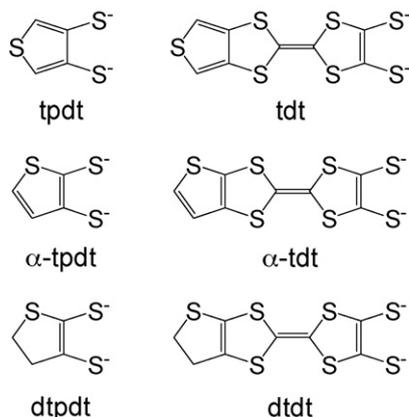
transport properties, ranging from metallic [14,15] to spin-ladder behaviour [16]. As in the corresponding organic donors both the sulphur atom position on the thiophenic ring and the aromaticity of the ligands can be changed in the inorganic complexes. The possibility to change the transition metal, and its oxidation state, confers to the inorganic complexes additional degrees of freedom in the application of these structural units to prepare molecular materials.

The following section will be dedicated to the small transition metal thiophenic dithiolenes based on the ligands α -tpdt, tpdt and dtpdt, with different transition metals (Au, Ni, Cu, Co, Pt, Fe...), which indeed exhibit rather low oxidation potentials and various values of the magnetic moment. Among these new small thiophenic complexes two of them attracted special attention.

The first one is the paramagnetic neutral complex $[\text{Au}(\alpha\text{-tpdt})_2]^0$ (**15**) that was found to display highly conducting metallic properties [13a], being among the first examples of a new type of molecular conductors based only on a neutral molecular species, the so called “single component molecular metals” (SCMM) [17]. These new type of conductors, in contrast to all previously known molecular conductors, are composed by a single neutral molecule and not by a pair of donor/acceptor molecules, and provided a new paradigm of molecular metals. The semimetallic nature of SCMM is thought to result from a partial overlap of the HOMO and LUMO bands predicted to be possible with small HOMO–LUMO gap molecules.

The other special complex is the paramagnetic anion $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ (**12**). This has been extensively used as a building block to prepare different molecular magnetic compounds, with magnetic properties ranging from metamagnets to cluster-glass behaviour [18].

Following the discovery of SCMM properties in $\text{Au}(\alpha\text{-tpdt})_2$ (**15**) a next approach was naturally developed, with a focus on the synthesis of similar transition metal complexes based on more extended dithiophene ligands with TTF moieties. This approach aims at combining the functionalities of the two first examples of SCMM in the same molecule [13a,17a]. The first transition metal complexes based on the highly extended dithiophene ligands tdt (3-({5-[(2-cyanoethyl)thio]-2-thieno[3,4-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile), dttd (3-({5-[(2-cyanoethyl)thio]-2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile) and α -tdt (3-({5-[(2-cyanoethyl)thio]-2-thieno[2,3-d][1,3]dithiol-2-ylidene-1,3-dithiol-4-yl}thio)propanenitrile) (Scheme 4) were recently reported [19]. The complexes with these new ligands are in general highly conducting in the neutral state thus providing new examples of the still rare class of SCMM [19b]. This will be presented in greater detail in Section 3.



Scheme 4.

2. Complexes based on simple conjugated fused thiophene-dithiolate ligands

2.1. Synthesis and redox behaviour

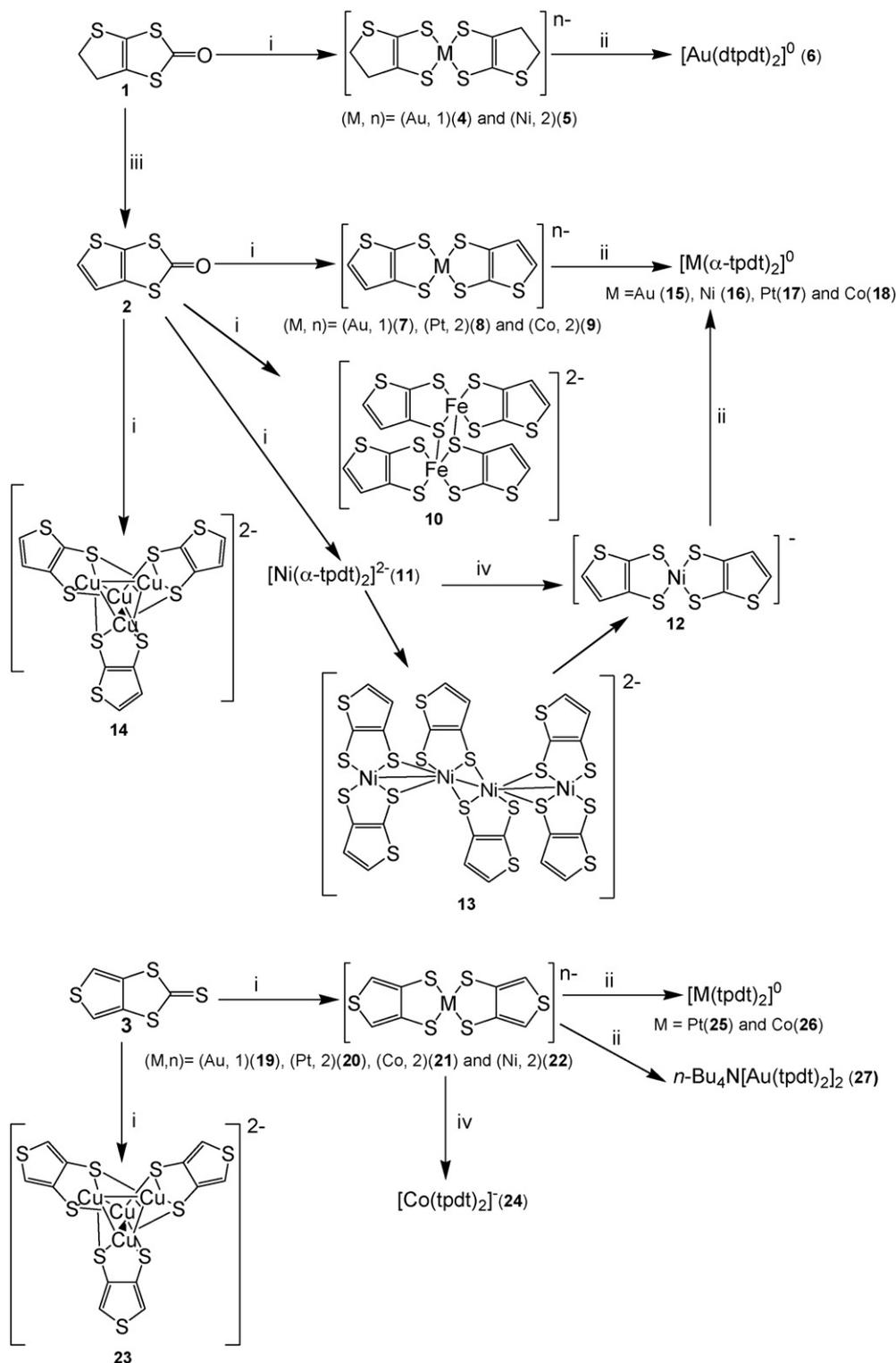
The first metal complexes reported with fused thiophene-dithiolate ligands, α -tpdt, dtpdt, and tpdt, were the gold complexes obtained as tetrabutylammonium salts. Subsequently, similar bithiophene-dithiolate complexes with different transition metals, such as Ni, Cu, Co, Pt and Fe have been prepared and explored. The ligand precursor in the synthesis of the complexes with the dtpdt, α -tpdt and tpdt ligands were, respectively, the 5,6-dihydrothieno[2,3-d]-1,3-dithiol-2-one (**1**) [20], its aromatic analogue the 5,6-thieno[2,3-d]-1,3-dithiol-2-one (**2**) and the aromatic thieno[3,4-d]-1,3-dithiol-2-thione (**3**) [21]. The starting compounds **1** and **3** were already known, and compound **2** was obtained in high yield by aromatisation of **1** by refluxing with DDQ in toluene [13a]. The syntheses of all the complexes were performed following a common procedure in strictly anaerobic conditions inside a glove box (Scheme 5). The thiophene-dithiolate ligands in solution were obtained from the corresponding ligand precursor by hydrolytic cleavage with potassium methoxide in methanol solution. These ligands, without intermediate isolation, were immediately reacted with the appropriate metal chloride to give the monoanionic Au (**4**, **7**, **19**) [13a] and Fe (**10**) complexes [13c], or the dianionic complexes in the case of the Co (**9**, **21**), Pt (**8**, **20**) and Cu (**14**, **23**) [13b]. The Au and Fe complexes were precipitated as tetrabutylammonium (*n*-Bu₄N) salts and the Co, Pt and Cu complexes as tetraphenylphosphonium (TPP) salts, by treatment with *n*-Bu₄NBr or TPPBr, respectively. The use of larger cations, such as TPP, was found to facilitate the crystallisation process of some of the salts.

The monoanionic $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ complex (**12**) was obtained as *n*-Bu₄N salt, following the described methodology, using *n*-Bu₄NI instead of *n*-Bu₄NBr. The Ni complex was isolated after stirring the reactional solution under air on a bath at 0 °C [18a]. The monoanionic $[\text{Co}(\text{tpdt})_2]^-$ (**24**) complex was also obtained as a TPP salt simply by stirring under air an acetonitrile solution of **21** [13b]. The TPP₂[Pt(α -tpdt)₂](**8**) salt in acetonitrile solution changes colour to green when exposed to air, indicating that an oxidation process takes place. However, it was not possible to isolate the monoanionic complex, possibly due to decomposition and instability of the Pt(III) complexes [13b]. The Fe complex was obtained only with the α -tpdt ligand, in the usual dimerised configuration $[\text{Fe}(\alpha\text{-tpdt})_2]_2^{2-}$. In addition to the *n*-Bu₄N salt, following the same methodology, this Fe complex was also obtained as tetraethylammonium (TEA) and 1-(4'-bromobenzyl)pyridinium (BrBzPy) salts [13c].

After recrystallisation in acetone-isopropanol all compounds gave air stable crystals with yields in the range 50–80%. The best crystal for single crystal X-ray diffraction studies were obtained by slow evaporation of acetonitrile solutions. Although not exhaustively tested, the synthesis yields did not change significantly by the use of thione instead of ketone precursors.

The $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ complex, by far the most explored anion in these families, has been isolated as salts with different types of cations. The synthetic procedure described above was also used in the preparation of salts with cations 1-(4'-halogenbenzyl)pyridinium (HalBzPy) [18b] and crown-ether types. For salts with cations of different nature, namely bearing spin-crossover (SCO) properties [18e] or decamethylmetalloceniums ($\text{M}(\text{Cp}^*)_2$) [18a,c,d] a slightly different method was used: **12** was first isolated and then combined with the salt of the desired cation via metathesis reaction in acetonitrile solutions.

With exception of **27**, where only a partial oxidation was achieved, consistent with a stoichiometry close to 1:2, all the other Au, Ni, Co and Pt anionic complexes were oxidised by iodine in



Scheme 5. Preparation of transition metal complexes with thiophene-dithiolene ligands **4–27**: (i) MeO–K⁺/MeOH, KAuCl₄ (**4**, **7**, **19**), NiCl₂·6H₂O (**5**, **11**, **22**), NaPtCl₄·3H₂O (**8**, **20**), CoCl₂·6H₂O (**9**, **21**), FeCl₃ (**10**) or CuCl₂·2H₂O (**14**, **23**) in MeOH, *n*-Bu₄NBr (**4**, **5**, **7**, **10**, **11**, **19**, **22**, **21**) or TTPBr (**8**, **9**, **14**, **20**, **23**) in MeOH; (ii) I₂ in acetone; (iii) DDQ in toluene; (iv) air exposure.

acetone solutions, to the corresponding neutral complex. The same products were also obtained by electrochemical oxidation. Despite the use of different crystallisation techniques, so far no single crystals of the neutral complex, nor of **27**, could be obtained. Compounds **6**, **15–18** and **25–27** were always obtained as a very fine dark microcrystalline powder [13a]. The very low solubility of the neutral complexes in virtually all solvents tested, with exception of

nitrobenzene where they are only slightly soluble, has so far prevented the growth of single crystals suitable for X-ray structure determination.

The above mentioned stability of the different transition metal bithiophene-dithiolate complexes is consistent with their redox behaviour investigated by electrochemical studies. Cyclic voltammetry studies of all complexes were carried out in acetonitrile and

Table 1
Redox potentials of complexes **4**, **5**, **7–9**, **11**, **14**, **19**, **20**, **22–24**, measured in acetonitrile vs. Ag/AgCl.

Compound	$E_{1/2}$ (mV) ($ML_2^{3-} \rightarrow ML_2^{2-}$)	$E_{1/2}$ (mV) ($ML_2^{2-} \rightarrow ML_2^{-}$)	$E_{1/2}$ (mV) ($ML_2^{-} \rightarrow ML_2^0$)	Ref.
<i>n</i> -Bu ₄ N[Au(tpdt) ₂] (19)		−900	+754 ^a /+1319	[13a]
<i>n</i> -Bu ₄ N[Au(α-tpdt) ₂] (7)		−1162	+456	[13a]
<i>n</i> -Bu ₄ N[Au(dtpdt) ₂] (4)		–	+201	[13a]
<i>n</i> -Bu ₄ N[Ni(tpdt) ₂] (22)		–	+450/+670 ^b	Unpublished
<i>n</i> -Bu ₄ N[Ni(α-tpdt) ₂] (11)		−562	+253	[18a]
<i>n</i> -Bu ₄ N[Ni(dtpdt) ₂] (5)		−562	+240	Unpublished
TPP ₂ [Pt(tpdt) ₂] (20)		−253	+416	[13b]
TPP ₂ [Pt(α-tpdt) ₂] (8)		−519	+69/+152/+278 ^b	[13b]
TPP[Co(tpdt) ₂] (21)		−618	+497	[13b]
TPP ₂ [Co(α-tpdt) ₂] (9)		−591	−257/−175/−8 ^b	[13b]
TPP ₂ [Cu ₄ (tpdt) ₃] (23)	−330	+148/+293 ^b	–	[13b]
TPP ₂ [Cu ₄ (α-tpdt) ₃] (14)	−506/−278 ^b	+182/+430 ^b	–	[13b]

^a $M^{III} \rightarrow M^{III/IV}$.

^b Processes occurring in more than one stage.

the redox potential values vs. Ag/AgCl of the different processes observed are listed in Table 1.

In general these transition metal complexes with thiophene-dithiolate ligands present lower oxidation potentials when compared with complexes with simple bisdithiolene ligands such as mnt or even bdt (benzodithiolate). With exception of the copper complexes which present a different coordination, when going from tpdt to α-tpdt ligands the redox potentials decrease showing an increasing facility of the anionic complexes to be oxidised to the neutral species. The non-aromatic complexes with.dtpdt ligands are even easier to oxidise.

2.2. Crystal and molecular structures

The usual square planar geometry of transition metal bisdithiolene complexes was found both in the monoanionic and dianionic species of the Au, Co, Pt and most of the Ni complexes with dithiophene ligands (Fig. 1a) [13a,b] [18]. Three relevant exceptions to this geometry were found.

The $[Fe(\alpha\text{-tpdt})_2]^{2-}$ dianions exhibit the usual square pyramidal, 4 + 1, coordination geometry due to the formation of dimeric arrangements through two Fe–S bonds between distorted square based $[Fe(S_2L)_2]^-$ units. These units are characterised by having each iron atom with 4 basal Fe–S bonds and one apical Fe–S bonds (Fig. 1b). In one particular case, this geometry is favoured by an efficient stacking of the anions induced by the cations [13c].

The copper complexes **14** and **23** were always obtained as a cluster of four metals with three ligands. In these complexes the dianion is composed by a four Cu(I) bonded centre [13b]. Three of the Cu

atoms are chelated directly to one dithiophene ligand and to an extra sulphur atom from a neighbouring ligand. The fourth Cu atom is also coordinated to 3 sulphur atoms, each one belonging to different dithiophene ligands (Fig. 1c). This coordination geometry, was previously known in a few $Cu_4(\text{dithiolates})_3^{2-}$ complexes [22]. In these previously reported examples the metal to ligand stoichiometry is controlled by the metal–ligand ratio during the synthesis, the ligand excess favouring the formation of the square planar Cu(II) complex. However in the present case, even employing a large excess of the ligands, the square planar Cu complex could never be obtained.

Another unexpected coordination geometry was found for Ni with the α-tpdt ligand in salts with crown-ether type cations, consisting in a unique Ni₄ dianionic cluster: $[Ni_4(\alpha\text{-tpdt})_6]^{2-}$. In this centrosymmetrical in-line Ni₄ dianionic cluster the peripheral nickel atoms, in addition to a square planar MS₄ coordination, are bound to a Ni atom (Ni–Ni, 2.75 Å), while the inner Ni atoms in addition to two Ni–Ni bonds (2.75 and 3.14 Å) are coordinated by 5 sulphur atoms two form an inner dithiophene ligand and three extra sulphur atoms belonging to different neighbouring ligands (Fig. 1d) [23]. This zigzag cluster can be understood as a dimer of Ni₂(α-tpdt)₃ units, similar to some previously described Ni₂(dithiolene)₃ units [24] in which two ligands coordinate to one nickel atom to form a square planar bidithiolene complex and another Ni atom is doubly coordinated by a ligand.

Although not isostructural, compounds **8**, **9**, **14**, **20**, **21**, **23** present quite similar crystal packing consisting of isolated anions surrounded by the TPP cations. Apart from some charge assisted, S⋯H, cation–anion hydrogen bonds, there is no other intermolecular contact [13b]. The crystal structure is not affected by changing the thiophenic sulphur atom position on the ligand. The α-tpdt ligand in these TPP salts was found to present always a disorder in the orientation of the thiophenic sulphur making it impossible to distinguish between a *cis* or *trans* conformation of the complex (Fig. 2).

However this disorder was not found in the *n*-Bu₄N salts of the monoanionic complexes (**4**, **7**, **19**, **12**) where both the.dtpdt and α-tpdt complexes were found to crystallise in the *trans* configuration [13a]. This suggests that the observed disorder is most likely the result of orientation disorder of the complex in the *trans* configuration. In the monoanionic *n*-Bu₄N salts, the hydrogen bonds and the strong S⋯S contacts involving the thiophenic ring favour the *trans* configuration preventing possible orientation disorder of the complex in those structures. Their crystal structure consists in alternated layers of cations and anions. The main difference between the packing is in the anionic arrangement within the layer. While in tpdt complexes the anions are arranged in linear chains in the case of the.dtpdt and α-tpdt complexes, the anions are arranged in zigzag chains as shown in Fig. 3.

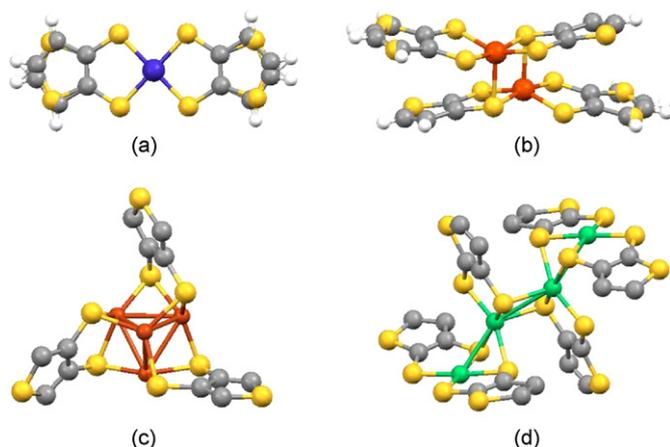


Fig. 1. Molecular coordination geometry types found in complexes **4–27**. (a) Square planar; (b) dimeric $[Fe(L)_2]^{2-}$ units; (c) $[Cu_4(L)_3]^{2-}$ cluster; (d) $[Ni_4(L)_6]^{2-}$ cluster.

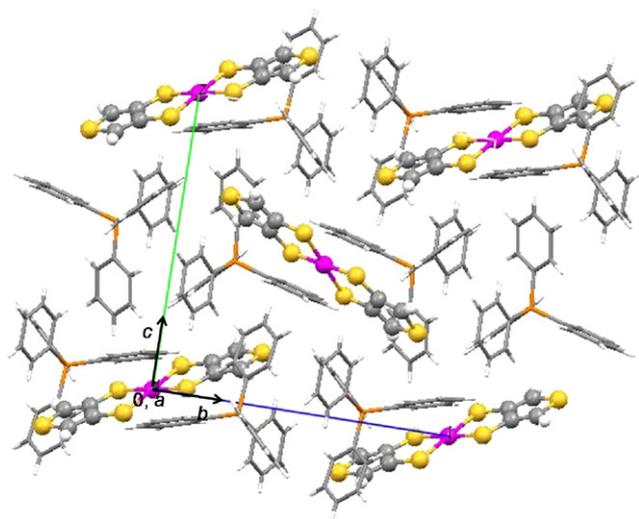


Fig. 2. Crystal structure of **20** viewed along *a*.

Among these complexes the most explored and studied one has been the $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ anion. In all its salts, although with different crystal packing motifs, the $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ anions always pack in a layered structure, composed by anionic zigzag type chains (Fig. 4) [18]. In these chains the key crystal engineering parameters concerning anion–anion interactions are the $\text{C} \cdots \text{S}$ interactions and the charge assisted hydrogen bonds, mediated by the peripheral thiophenic sulphur atom. Another important feature seems to be the degree of *cis*–*trans*/orientation disorder in the position of the terminal thiophenic sulphur atom. This degree of disorder is correlated with the strength of the interactions with the surrounding cations. These contacts can be of two types: hydrogen bonds involving the anion sulphur atoms or halogen atoms from the cations and aromatic π – π interactions. As the terminal thiophenic ring is aromatic, when the cations contain an aromatic system, the molecules in the crystal packing tend to arrange in order to maximise the π – π interactions. This cation–anion interaction is a crucial factor in order to stabilise the anion in the most favourable *trans* geometry.

The salts with the $[\text{Fe}(\alpha\text{-tpdt})_2]_2^{2-}$ dimers present significant differences on their crystal structures depending on the cation nature. In the Et_4N salt, as in **4**, **11** and **19**, a clear segregation between the two species is observed, leading to an alternated cationic–anionic layered crystal structure. The *n*- Bu_4N cation leads to a packing where isolated anions are surrounded by cations while the BrBzPy cation perfectly matching the widths of the anion, leads to a crystal structure made of parallel alternated columns of cations and anions [13c].

2.3. Magnetic properties

Some of these complexes are paramagnetic and have been used as active building blocks in new molecular magnetic materials. Among these anionic complexes the $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ has attracted special attention and this small paramagnetic, $S = \frac{1}{2}$ anion, has been at the basis of several families of new molecular materials with interesting magnetic properties. In this complex, due to the large ligand contribution to the frontier orbitals, the magnetic moment of these paramagnetic units is not fully localised in the metal and the complex presents a significant spin polarisation all over the complex. This was confirmed by DFT calculations, performed using the experimentally determined molecular geometry, which predict the spin density map that is showed in Fig. 5 [18c].

As a consequence of this spin distribution the solid state magnetic interactions are very sensitive both to the type of inter-

molecular contact and to the molecular overlapping geometry, leading to a clear correlation between the crystal structure motif and the magnetic behaviour of these materials. Considering this fact and in order to induce different intermolecular packing motifs, a considerable number of salts of this anion with a variety of cations with different shapes, volumes and dominant type of induced intermolecular interactions, either diamagnetic or paramagnetic, have been prepared during recent years. Although the crystal structures remain in general unpredictable some structural types are known to be induced by the anion and/or cation molecule, due to specific dominant cation–cation or anion–cation interactions. On that basis a set of different cations, ranging from the non-magnetic substituted benzylpyridinium [18b] or crown-ether based cations to the magnetic decamethylmetallocenium cations $(\text{M}(\text{Cp}^*)_2)$ [18a,c,d] or spin-crossover (SCO) Fe(III) complexes [18e] have been combined with the anion $[\text{Ni}(\alpha\text{-tpdt})_2]^-$. In all these salts the $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ anions, showed a common pattern which is a layered structure, composed by zigzag type chains dominated by $\text{S} \cdots \text{S}$ and $\text{C} \cdots \text{S}$ intermolecular interactions. Due to the spin polarisa-

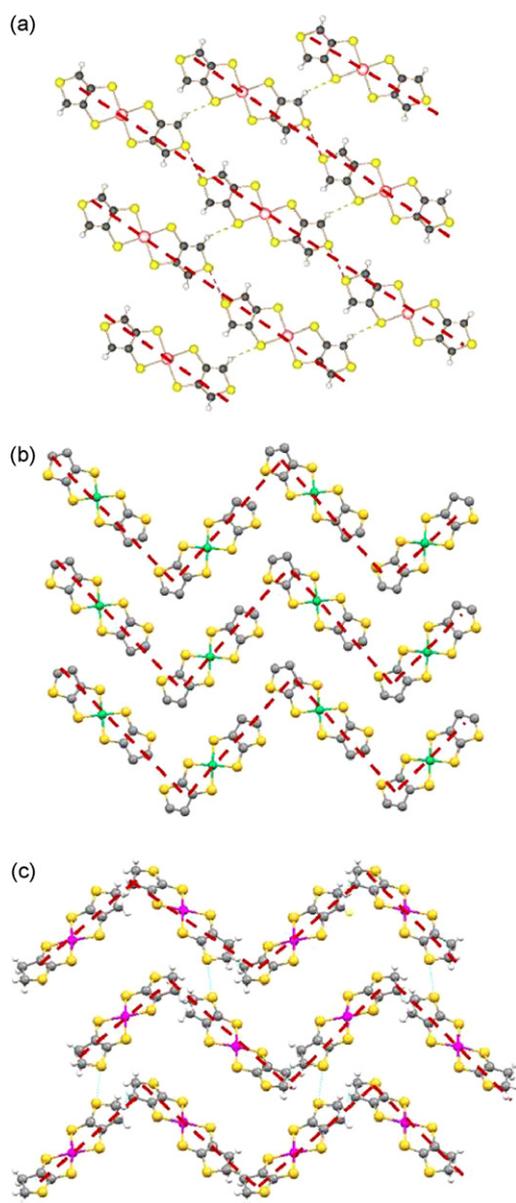


Fig. 3. Anionic layers in the crystal structures of (a) **19**, (b) **12** and (c) **4**. The red dashed line show the direction of the shorter interactions between anions, defining the anionic chains within the layers.

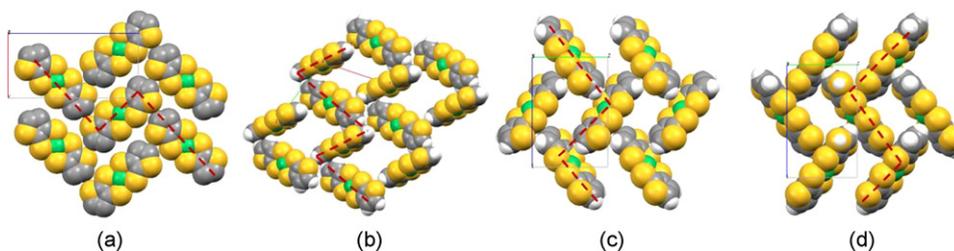


Fig. 4. Anionic $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ layers in (a) **12**, (b) $[\text{Fe}(\text{Cl-5-qsal})_2][\text{Ni}(\alpha\text{-tpdt})_2]$, (c) $[\text{Fe}(\text{Cp}^*)][\text{Ni}(\alpha\text{-tpdt})_2]$ and (d) $\text{RBzPy}[\text{Ni}(\alpha\text{-tpdt})_2]$. The red dashed line show the direction of the shorter interactions between anions, defining the anionic chains within the layers.

tion in the thiophenic ring there is a competition between AFM and FM interactions, but in most cases these interactions are predominantly ferromagnetic. Another important feature is the degree of *cis-trans*/orientation disorder in the position of the terminal thiophenic sulphur atom that in some cases prevents long range order resulting in magnetic properties such as cluster-glass behaviour. The degree of this disorder is correlated with the strength of the interactions with the surrounding cations.

In the case of salts with decamethylmetalloccenium paramagnetic cations there is a complex crystal structure with several cation–anion and anion–anion contacts resulting in a unique combination of single ion anisotropy with anisotropic intermolecular magnetic interactions [25].

Although in this family of compounds the crystal packing where found to be similar, different magnetic behaviours were observed which were ascribed to the different magnetic moments and single ion anisotropy of the cations. The common crystal packing pattern of these salts can be described as composed of alternating layers each consisting of parallel mixed donor–acceptor chains, with the chains in adjacent layers being perpendicular. The McConnell I model was used to analyse the intermolecular magnetic coupling in these structures and it predicts dominant ferromagnetic (FM) intra-chain coupling and antiferromagnetic (AFM) interchain coupling (both intra- and interlayer) [18c].

The Cr salt with no magnetic anisotropy remains paramagnetic down to 1.6 K, while the ferrocenium salt presents a metamagnetic behaviour below *ca.* 2.4 K with a critical field of 600 G at 2 K (Fig. 6), and the Mn compound presents a behaviour typical of a frustrated magnet with a blocking temperature of *ca.* 4 K. In this compound, the magnetic frustration results from a degenerate ground state in the interlayer spin arrangements. In both Fe and Mn compounds a rather unusual inverted hysteresis loop with negative remanence is observed (Fig. 7). This effect is associated with the layered structure of these compounds, together with the considerable magnetic anisotropy of the cations, being the first examples of bulk molecule based materials displaying such inverted hysteresis loops [18d].

The neutral gold complexes are also expected to be paramagnetic. This was confirmed by EPR studies and magnetic

susceptibility measurements. However the paramagnetic susceptibility at room temperature is rather small, particularly in the case of $\text{Au}(\alpha\text{-tpdt})_2$. In this case the small paramagnetic susceptibility is almost temperature independent in a wide temperature range, with a negligible Curie tail and a behaviour reminiscent of the Pauli paramagnetic susceptibility of metallic systems, consistent with the high conductivity of this compound as described below (Fig. 8).

Another promising paramagnetic building block is $[\text{Co}(\text{tpdt})_2]$ complex, although it is not yet much explored. Preliminary magnetic studies shows that this Co compound is in a high spin $S = 1$ state [23].

2.4. Electrical transport properties

Due to the difficulties in obtaining single crystals the electrical transport properties of the neutral complexes were measured in polycrystalline samples made of compressed powder pellets. Room temperature electrical conductivity, σ , measurements in these samples indicate values of the order of 10^{-9} S/cm for **27**, $3.3 \times 10^{-6} \text{ S/cm}$ for **6** and 7 S/cm for **15**. The electrical conductivity of **15** is quite remarkable, because in spite of its activated behaviour, as expected in a polycrystalline sample due to the interparticle resistance effects, the conductivity value is quite high for a polycrystalline sample. A detailed analysis shows that the temperature dependence of the electrical conductivity does not have a simple activation energy, the values of the derivative $d \ln \sigma / d(1/T)$ being quite small and ranging from 19.5 meV at room temperature to 3.5 meV at 20 K (Fig. 9). An additional indication that the material is intrinsically conductive with metallic properties is provided by the thermoelectric power. This property as a zero electrical current measurement is not so sensitive to the intercrystalline boundary

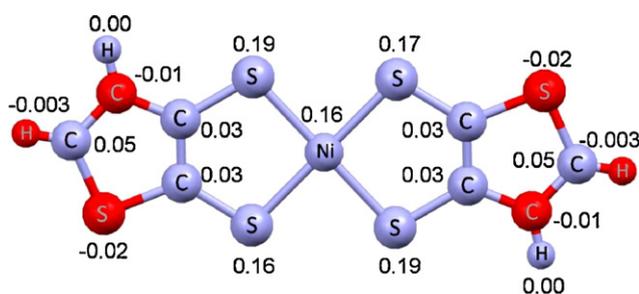


Fig. 5. Atomic spin density (ρ_s) distribution in the $[\text{Ni}(\alpha\text{-tpdt})_2]^-$ anion from Mulliken population analysis on the wave function obtained by B3LYP density functional computations [18c]. The atoms exhibiting a negative ρ_s are represented in red, while those with a positive ρ_s are represented in blue.

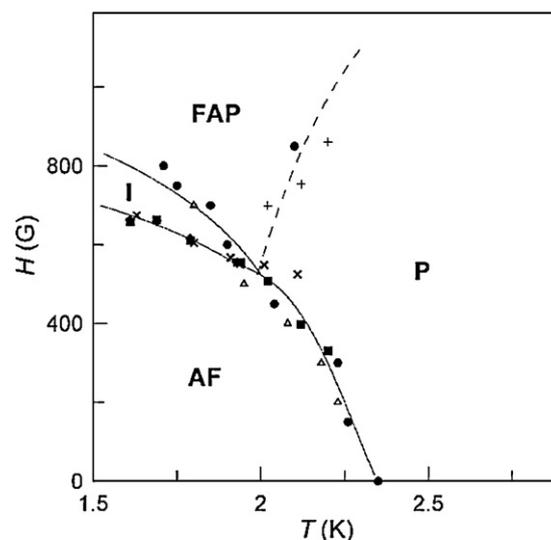


Fig. 6. (a) Magnetic phase diagram of $[\text{Fe}(\text{Cp}^*)][\text{Ni}(\alpha\text{-tpdt})_2]$ [from Ref. 18d].

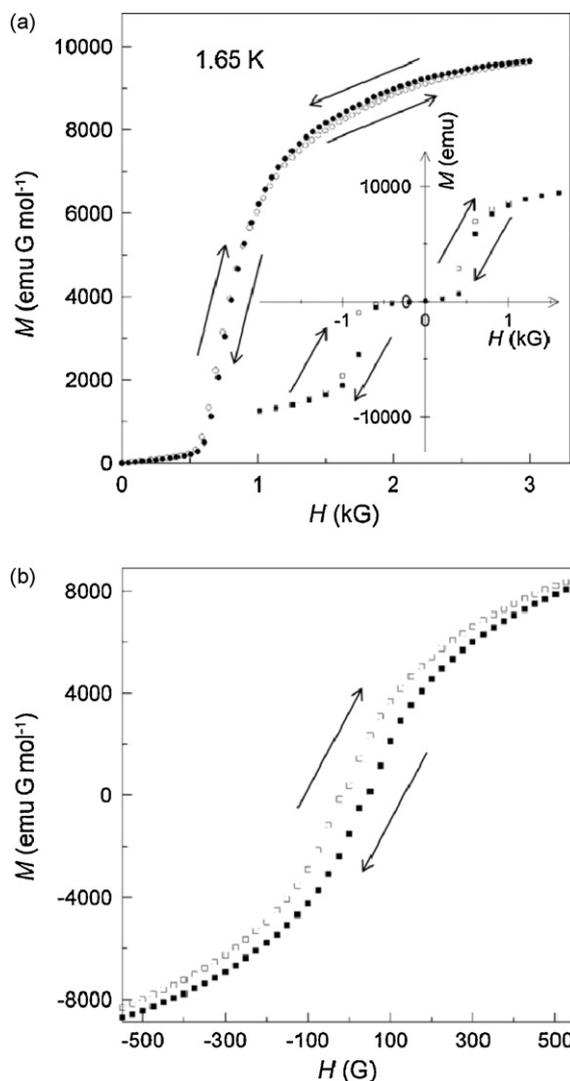


Fig. 7. (a) Magnetisation hysteresis loop (1.65 K) of compound $[\text{Fe}(\text{Cp}^*)][\text{Ni}(\alpha\text{-tpdt})_2]$ obtained between 0 and 3 kG. The inset shows a detail between -10 and 10 kG; (b). Detail of the inverted hysteresis loop of $[\text{Mn}(\text{Cp}^*)][\text{Ni}(\alpha\text{-tpdt})_2]$, at 1.65 K [from Ref. 18d].

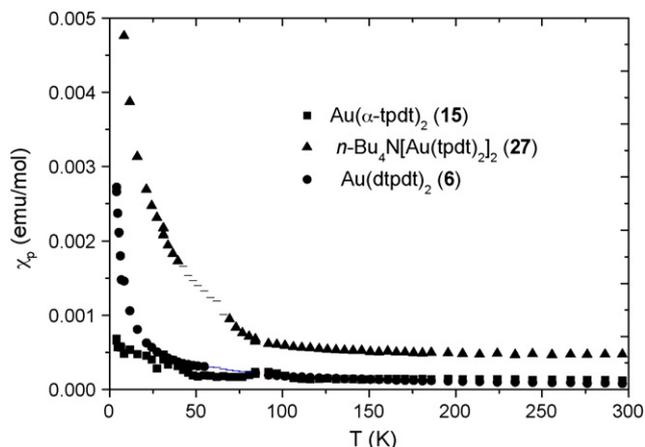


Fig. 8. Temperature dependence of the paramagnetic susceptibility, χ_p , of compounds **6** (●), **15** (■) and **27** (▲).

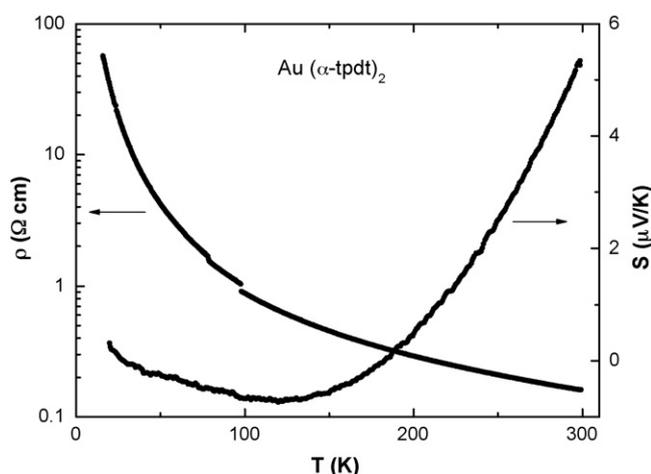


Fig. 9. (left) Electrical resistivity, ρ , and (right) absolute thermoelectric power of a polycrystalline sample of **15** as a function of temperature.

effects, and probes more directly the intrinsic properties of the material at variance with the electrical resistivity that is dominated by interparticle resistance effects. The thermopower data obtained in $\text{Au}(\alpha\text{-tpdt})_2$ compressed pellets (Fig. 9) shows very small values in all the temperature range between 15 and 300 K, with a maximum of $5.5 \mu\text{V/K}$ at room temperature. Not only the small magnitude of the thermopower data is typical of a metal, but also its temperature dependence, approaching zero upon cooling at lower temperatures, with a linear behaviour between 100 and 20 K, is clearly indicative of a system with the Fermi level lying in a continuum of states. In spite of the absence of single crystals this data provided the evidence for the first molecular metal based on a neutral species [13a].

Transport properties were also measured in the neutral complexes with other metals. As in the gold complexes no single crystals were obtained and the studies were done in polycrystalline samples. However the measurements of the electrical conductivity in these samples always indicated conductivities lower than 10^{-6} S/cm .

Without a crystal structure determination it remains unclear the structural features responsible for the unique high conductivity of the $\text{Au}(\alpha\text{-tpdt})_2$ neutral complex when compared with Au complexes with other thiophene-dithiolene ligands or with other metals, which are essentially insulating. In any case, the high conductivity of the $\text{Au}(\alpha\text{-tpdt})_2$ neutral complex must result from a partial overlap of the HOMO and LUMO bands, leading to a semimetallic situation of two partially filled bands. This situation is possible due to the small HOMO–LUMO gap and may be also favoured by quite 3D interactions made possible by the relatively sulphur rich nature of the ligands.

3. Complexes based on extended dithiothiophene ligands

The peculiar transport properties of the $\text{Au}(\alpha\text{-tpdt})_2$ neutral complex stimulated the exploration of similar transition metal complexes with more extended dithiothiophene ligands. Efforts were directed towards new ligands (tdt, $\alpha\text{-tdt}$ and dtdt) which besides the terminal thiophenic group also incorporate a TTF moiety combining in the same molecule the “functionalities” of the two first examples of SCMM (Scheme 4): the $\text{Au}(\alpha\text{-tpdt})_2$ [13a] and $\text{Ni}(\text{tmdt})_2$ [17]. These new extended dithiothiophene ligands are expected to provide complexes with lower HOMO–LUMO gaps, as confirmed by molecular orbital calculations, and their sulphur rich nature will certainly allows the establishment of extended networks of $\text{S} \cdots \text{S}$ interactions in the solid state.

3.1. Synthesis and redox behaviour

The synthesis of the ligand precursors for these complexes followed a synthetic route first used by Underhill and co-workers [26], involving the cross-coupling between the ketones **1** and **2**, the ligand precursors of the simpler transition metal complexes described in Section 2, and thione **28** in the presence of trimethyl phosphate (Scheme 6) [19a]. The yields of the coupling reactions to obtain **29** and **30** are 20% and 28%, respectively. The tpdt ligand (Scheme 4) was also prepared by the same method, but remains so far less explored and its complexes have not been reported yet. These low yields reflect the coprecipitation of several by-products resulting mainly from the self-coupling of the reactants. Column chromatography, eluted with dichloromethane, was needed in order to separate this mixture. Single crystals suitable for RX measurements were obtained from slowly cooling dichloromethane/*n*-hexane saturated solutions [19a].

The syntheses of the gold, nickel and copper complexes were performed starting from these ligand precursors following a general common procedure (Scheme 6) under strictly anaerobic conditions in a one pot reaction [19b]. The extended dithiothiophene ligands, α -tdt and dtdt, were obtained in solution from the corresponding protected precursors **29** and **30**, by hydrolytic cleavage with *n*-Bu₄NOH, in a methanol/THF solution. These ligand solutions were immediately reacted with the desired metal chloride and subsequently precipitated as tetrabutylammonium salts. Crystallisation in dimethylformamide (DMF) affords air stable crystals. The preparation yields of the complexes range from 44 to 75%. Elemental analysis reveals a 1:1 cation to anion stoichiometry in the case of compounds **31**, **32**, **37** and **38**, also confirmed by the X-ray crystal structure analysis in single crystals in the case of gold complexes.

In the case of nickel complexes, and in spite of strict anaerobic conditions, elemental analysis often indicated a variable cation:anion stoichiometry, between 2:1 and 1:1, indicative of a mixture of the monoanionic and dianionic salts. The existence of the Ni monoanions is demonstrated by the EPR spectra of frozen solutions prepared from the obtained Ni complexes samples synthesised in the most stringent anaerobic conditions, showing the typical signal of the Ni(III) bisdithiolene complexes in a square planar coordination. Some single crystals of *n*-Bu₄N[Ni(α -tpdt)₂], suitable for X-ray analysis were obtained by recrystallisation from a DMF solution. However pure samples of Ni monoanionic complexes are difficult to isolate since, just by air exposure of solutions of these mixture samples, it is achieved the neutral complex as further explained below.

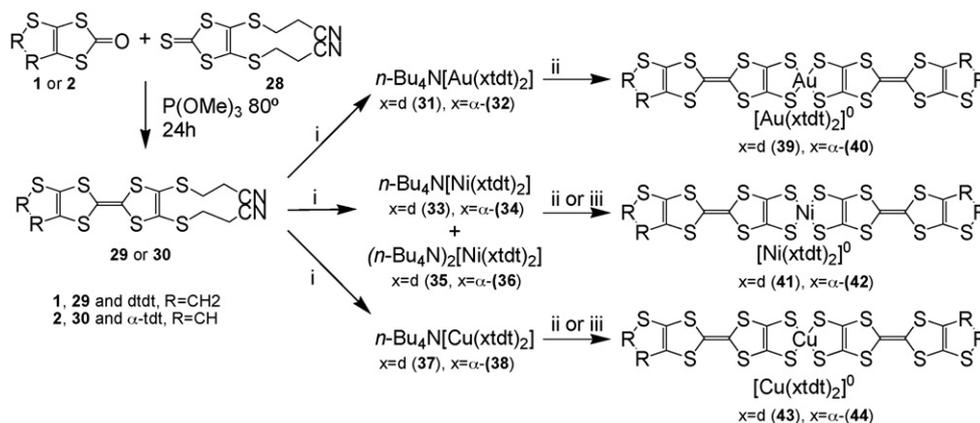
Compounds **39** and **40** were prepared from the corresponding anionic salts by oxidation, in DMF, with equimolar solutions of iodine or, in the case of compounds **41–44**, also by simply air exposure of those solutions. In all cases the neutral complexes were obtained as fine dark powder. The very low solubility of the neutral complexes in most of the solvents tested, with exception of thiophene, DMF and DMSO where the salts were only slightly soluble, has so far prevented the growth of single crystals suitable for X-ray structure determination. Powder X-ray diffraction studies of these samples, indicate a variable degree of crystalline that is correlated, with the oxidation procedure. Iodine oxidised samples show in general an almost completely amorphous nature, while Ni samples oxidised by slow air exposure, reveal a microcrystalline diffraction pattern.

Electrochemical studies can explain the different oxidation behaviour observed in these complexes. Redox potentials obtained by cyclic voltammetry are listed in Table 2. Although the redox behaviour of the Ni complexes is quite distinct from the Au ones, there are no significant differences between the complexes with the ligands dtdt and α -tdt.

The first redox process is ascribed to the couple $M(\text{xtdt})_2^{2-}/M(\text{xtdt})_2^-$ while the second process corresponds to the couple $M(\text{xtdt})_2^-/M(\text{xtdt})_2^0$. These low oxidation potentials explain why in both cases the anionic complexes are readily oxidised to the neutral state and are in agreement with the observed stability of the complexes upon their synthesis, as previously described. The low and closely spaced oxidation potentials in the Ni complexes are consistent with the difficulty on isolate the monoanion and with the observed instability of the (*n*-Bu₄N)_n[Ni(tpdt)₂] solutions that when exposed to air readily give rise to the neutral complex, as very 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 using a stronger oxidant such as iodine.

3.2. Crystal structures

The usual square planar coordination geometry was found in both gold and nickel monoanionic complexes with the extended dithiothiophene ligands [19b]. However in the case of the complexes with the aromatic α -tdt ligand a significant tetrahedral distortion was observed. All these long complexes are non-planar, with significant deviations from the average molecular plane (Fig. 10). The larger deviations are observed on the terminal parts of the ligands, associated to a bending in the TTF moiety, and the



Scheme 6. Preparation of transition metal complexes **31–44** (i) in THF at -78°C ; *n*-Bu₄NOH in MeOH/THF at -78°C ; RT; KAuCl₄ (**33** and **34**), NiCl₂·6H₂O (**35–38**) or CuCl₂·2H₂O (**39** and **40**) in MeOH/THF at -78°C ; (ii) I₂ in DMF; (iii) in DMF by air exposure.

Table 2
Redox potentials of complexes **31**–**36**, measured in DMF vs. Ag/AgCl.

Compound	$E_{1/2}$ (mV) ($ML_2^{2-} \rightarrow ML_2^{1-}$)	$E_{1/2}$ (mV) ($ML_2^{1-} \rightarrow ML_2^0$)	Ref.
<i>n</i> -Bu ₄ N[Au(dtdt) ₂] (31)	–754	+90	[19b]
<i>n</i> -Bu ₄ N[Au(α -tdt) ₂] (32)	–715	+110	[19b]
(<i>n</i> -Bu ₄ N) ₂ [Ni(dtdt) ₂] (35)	–448	–206	[19b]
(<i>n</i> -Bu ₄ N) ₂ [Ni(α -tdt) ₂] (36)	–411	–196	[19b]

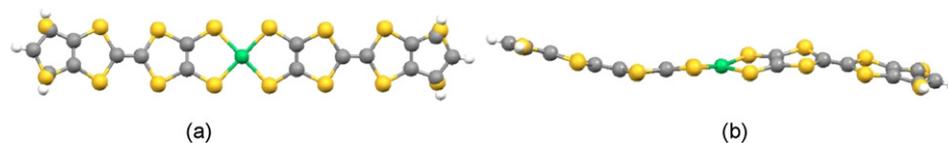


Fig. 10. Anion geometry observed in compound **34**: (a) top view and (b) side view.

complexes can present distortions from planarity adopting either boat-like or chair-like conformation, depending on the crystal environment.

As in the transition metal complexes with smaller dithiophene ligands a orientation disorder of the terminal thiophenic sulphur atoms of the α -tdt and dtdt ligands was also observed in these more extended complexes. As before it was impossible to distinguish between the *cis* and *trans* configurations, since both configurations with orientation disorder could give the observed results. However, because other bisdithiolenes incorporating thiophenic units were found to crystallise in the *trans* configuration [13a,b,18a], it is believed that in these cases the crystal structure disorder also results from a molecular orientation disorder of the complexes in the *trans* configuration.

Polymorphism seems to be generally present among these complexes. Both gold compounds showed two different structures as shown in Fig. 12 for **32** with and without a solvent molecule incorporated. A different unit cell was also observed in **31** [19b]. The Ni compound **34** is isostructural to the gold analogue **32**. Although not isostructural, all crystal structures present a similar packing pattern with a strong segregation of anions and cations in alternating layers. The anionic layers present a very dense 2D network of short S...S contacts. The link between anionic and cationic layers is achieved through several hydrogen bonds.

In all structures the anionic layers are composed of tightly packed parallel domino like chains of complexes. In these chains the overlapping modes between anions differs slightly from structure to structure. In the case of the anions with the α -tdt ligand, there is a prevalence for an effective overlapping between anions involving one half of the ligand, from half the TTF moiety to the thiophenic ring (Fig. 11b). However, in the case of the dtdt ligand the overlapping modes between the anions tend to be smaller, involving only the terminal thiophenic ring (Fig. 11a).

Parallel anionic chains are connected through several side-by-side short S...S contacts, involving all the type of sulphur atoms from thiophenic and TTF to coordination, originating an extended 2D network of contacts (Fig. 12).

In these crystal structures, due to the close packing and large number of sulphur atoms always involved in several short contacts, the position of the terminal thiophenic sulphur atom seems to be irrelevant. In both orientations the anions are close enough to

interact with the neighbours without rupture of the dense network of short contacts. The key crystal engineering parameters concerning anion–anion interactions are the S...S short side contacts and the π – π interactions maximised through the domino like chains arrangement allowing a more or less effective overlapping of the thiophenic and the TTF moieties.

The tendency to establish S...S short side contacts and the π – π interactions, maximised through the overlapping of the thiophenic rings, was already observed in the crystal structure of the ligand precursors [19a]. In both precursors (**29** and **30**) these molecules stack in head-to-tail fashion, with the cyanoethyl chains segregated from the TTF cores. These multi-sulphurated molecules tend to position side-by-side, in order to maximise the sulphur–sulphur interactions allowing the neighbouring stacks to interact through several S...S contacts. Along the stacks the thiophenic ring lays over the TTF ring, allowing the contact between the sulphur atoms and the π – π interactions between the aromatic rings.

3.3. Electronic transport properties

Four-probe electrical conductivity measurements were performed in compressed powder pellets of the neutral complexes. These measurements in polycrystalline samples are expected to be dominated by interparticle resistance possibly further enhanced by anisotropy effects. In the case of the nickel neutral complexes the transport properties were found to be sensitive to the oxidation procedure, giving different results depending if the anionic sample are oxidised by air exposure or with iodine.

Room temperature electrical conductivity data in these powder samples indicate values in the range of 2–8 S/cm for the Au, Cu and Ni neutral complexes obtained by iodine oxidation. The Ni microcrystalline samples, obtained by slow air exposure, present even higher electrical conductivity values of 200 and 24 S/cm for Ni(dtdt)₂ and Ni(α -tdt)₂, respectively (Fig. 13). Despite their powder nature, the electrical conductivity, σ , of these Ni microcrystalline samples increases upon cooling, showing a metallic behaviour ($d\sigma/dT < 0$), in a wide range of temperatures, comparable to that observed in the Ni(tmdt)₂ compound which was further characterised as single crystals. This “metallic” range of powder electrical conductivity, in the case of the highly conducting Ni(dtdt)₂ samples, extends down to 80 K (Fig. 14). It is worthwhile



Fig. 11. Domino like patterns of anion chains in the crystal structure of (a) **32** and (b) **33**.

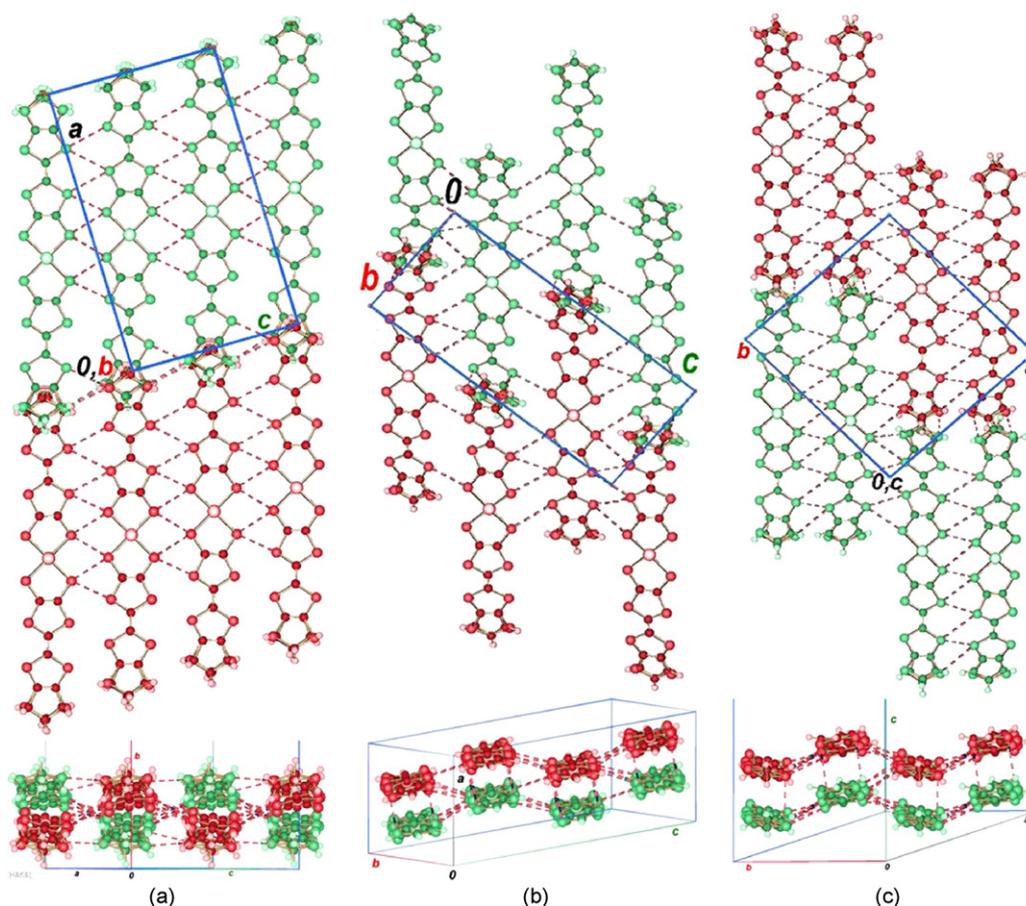


Fig. 12. Top and front views of the anionic layers in the crystal structure of (a) **31**, (b) **32** and (c) **32 DMF**. The dashed lines represent short S...S contacts [from Ref. 19b].

mentioning that, as previously pointed out for $[\text{Au}(\alpha\text{-tpdt})_2]$, even the complexes showing lower conductivity present exceptionally large conductivity for a polycrystalline sample, and for a compound based on a neutral component. The electrical conductivity activation energy of these compounds is also rather small (at most 20 meV at room temperature) and most probably reflects interparticle resistance effects [19b]. The copper analogues, although not yet studied in great detail, show comparable electrical transport properties (Fig. 13).

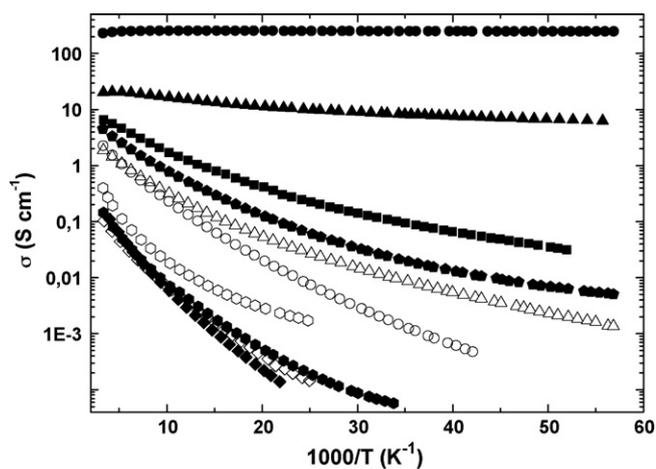


Fig. 13. Electrical conductivity, σ , of **39** (\blacklozenge), **40** (\blacksquare), **41** (\bullet : oxidation by air, \circ : iodine oxidation), **42** (\blacktriangle : oxidation by air, \triangle : iodine oxidation), **43** (\blacklozenge : oxidation by air, \diamond : iodine oxidation) and **44** (\bullet : -oxidation by air, \circ : -iodine oxidation) polycrystalline samples as a function of temperature T .

In the case of the nickel samples, thermopower measurements also show different behaviours depending on the oxidation procedure. In all cases the thermopower values are relatively small and compatible with molecular metals, but in the $\text{Ni}(\alpha\text{-tdt})_2$ samples, prepared by air oxidation, a behaviour typical of a simple metal is observed, with values decreasing almost linearly with the temperature [19b]. The behaviour observed in other cases is more likely the result of a multiband metallic system.

The room temperature electrical conductivity, σ , measured in a single crystal of gold compound **32**, was found to be

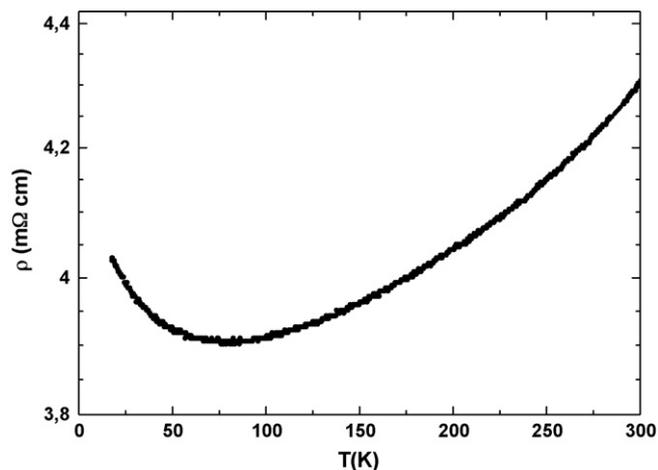


Fig. 14. Electrical resistivity, ρ , of **41** obtained by oxidation by air exposure, as a function of temperature, T [from Ref. 19b].

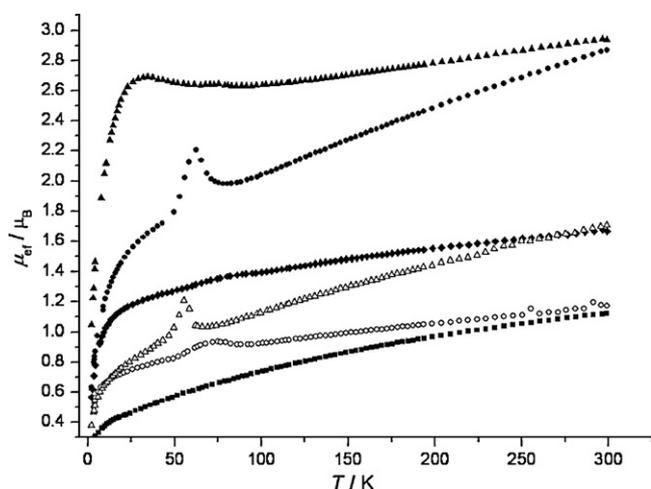


Fig. 15. Effective magnetic moment, μ_{eff} , of **39** (◆), **40** (■), **41** (●: oxidation by air exposure, ○: iodine oxidation) and **42** (▲: oxidation by air exposure, △: iodine oxidation) polycrystalline samples as a function of temperature T [from Ref. 19b].

$\sigma_{\text{RT}} = 10^{-4} \text{ S/cm}$. Although with a semiconducting behaviour this value is relatively large for a monoanionic $n\text{-Bu}_4\text{N}$ salt, confirming the exceptional capability of this extended thiophene-dithiole units to make extended interactions in the solid state.

3.4. Magnetic properties

The monoanionic Au bisdithiolenes complexes, as d^8 systems in a square planar coordination environment, are expected to be diamagnetic, and the oxidised neutral species are expected to be paramagnetic, while for the nickel complexes it is usually the opposite. Indeed the gold neutral complexes with dithiophene ligands present, in powder samples, a single EPR line 200 and 40 G wide and centred at $g = 1.94$ and $g = 2.0026$, which are already visible at room temperature, for **39** and **40**, respectively [19b]. The shape of these lines, as expected from the high electrical conductivity, show a strong Dysonian type asymmetry [27], typical of highly conducting systems. However, the neutral nickel complexes also present a similar EPR signal.

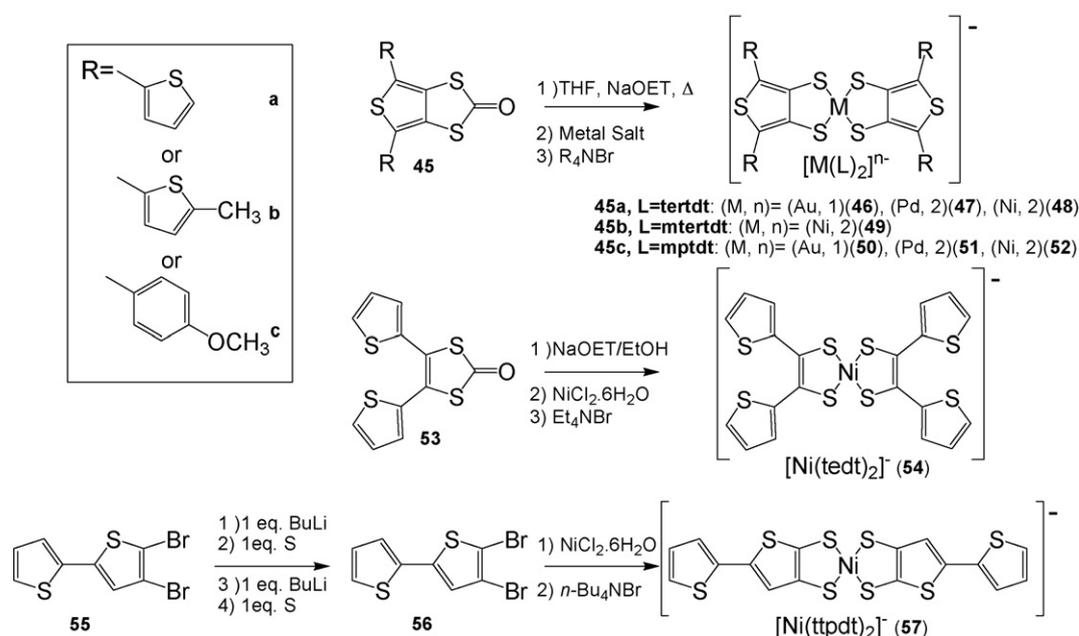
Static magnetic susceptibility measurements of the neutral complexes in the temperature range 4–300 K confirm their paramagnetic nature. However these measurements reveal rather large values of the effective magnetic moment, with a magnetic susceptibility much larger than the usual small Pauli contribution of the delocalised electrons as expected from the metallic properties (Fig. 15).

These large susceptibility values as shown in Fig. 15 correspond to effective magnetic moments in the range 1–3 μ_{B} at room temperature, slowly decreasing upon cooling. The unexpected large values indicate that these complexes are in a high spin state, most probably as a consequence of almost degenerated low lying orbitals. These results imply that in addition to the expected Pauli type contribution due to delocalised electrons in partially filled bands, these compounds have additional unpaired localised electrons responsible for the large susceptibility observed. This is an interesting new situation in molecular materials, which requires further studies namely theoretical calculations of the spin states.

4. Polymerisable thiophene-functionalised metal dithiolenes

This section describes transition metal dithiolenes functionalised with appended thiophene/aromatic groups, essentially uncoupled to the MS_4C_4 bisdithiolenes core, which have been prepared aiming essentially at obtaining transition metal complex polymeric materials by electropolymerisation [9–11]. This strategy was adopted after it was found that simple fused thiophene-dithiolenes based transition metal complexes, such as $\text{Ni}(\alpha\text{-tpdt})_2$ are not able to electropolymerise. This was attributed to the fact that the thiophene moiety is not sufficiently decoupled from the MS_4 centre to generate a reactive radical cation. The next strategies were naturally focused on the synthesis of dithiolenes ligands with more uncoupled appended thiophenic units. These transition metal complexes have been prepared following the same general synthetic methodologies usually followed in the preparation of bisdithiolates complexes, as summarised in Scheme 7.

The cyclic voltammetry studies of these new complexes are dominated by the formation of cathodic species, assigned to the



Scheme 7. Preparation routes of transition metal complexes **45–57**.

outer thiophenic units, and to the possibility of the formation of polymers, that in some cases was already confirmed [10,11]. In most cases the identity of these complexes could be confirmed by X-ray diffraction studies of single crystals. The molecular crystal structures reveal in all cases the usual square planar geometry and it was also found that the appended thiophenic and other outer aromatic units are tilted relatively to the planar metal central core. The review by S. Dalglish and N. Robertson in this issue will cover in detail the synthetic, structural and physical properties of these compounds [12].

5. Conclusions

The complexes of different transition metals based on thiophene-dithiolene ligands emerged as a research topic only about 10 years ago and they are still far from being well explored. However it is already clear from the above mentioned examples that the thiophene rings fused to the dithiolene group lead to a series of fairly extended π -ligands, which significantly lower the oxidation potentials of the corresponding transition metal complexes and enabling the establishment of strong $S \cdots S$ interactions in solid state. In many cases this decrease in the oxidation potentials makes it possible to isolate the complexes in the neutral state. Due to the low HOMO–LUMO gap and 3D $S \cdots S$ interactions the neutral complexes can present metallic properties and are new examples of SCMM. The study of these new SCMM has been however limited by the difficulty in crystallising these compounds due to their low solubility.

A remarkable structural diversity is observed in the complexes based on thiophene-dithiolene ligands, in which besides the usual square planar coordination geometry, pyramidal Cu_4 and in-line Ni_4 clusters are also observed.

The paramagnetic thiophene-dithiolene complexes are currently being explored and have already provided interesting molecular magnetic materials. The magnetic properties of the salts based on complexes with small ligands like the paramagnetic $[Ni(\alpha\text{-tpdt})_2]^-$ anion are now fairly well understood. However the salts of complexes with other metals, namely $[Co(tpdt)_2]^-$ on a high spin state, are not yet explored. The magnetism of the complexes based on more extended ligands, which seem to easily adopt high spin configurations, is presently also only very poorly explored.

Further research on these complexes during the next few years, namely on other metal/ligand combinations not yet tested and additional studies such as theoretical quantum chemical calculations, are expected to enlarge the potential of these complexes as useful building blocks in the preparation of molecular materials with novel electric and magnetic properties.

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