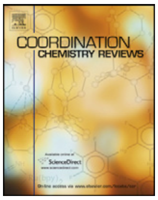
Coordination Chemistry Reviews 254 (2010) 1493–1508

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Dithiolene complexes containing N coordinating groups and corresponding tetrathiafulvalene donors

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Contents

Abbreviations: 18C6, 18-crown-6-ether; 15C5, 15-crown-5-ether; *adt*, 2-cyano-1,2-ethanedithiolate; AcOH, acetic acid; B15C5, benzo-15-crown-5-ether; BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene; *bpedmit*, 4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-thione; *bpmdmit*, 4,5-bis(2-pyridylmethylsulfanyl)-1,3-dithiole-2-thione; BVDT-TTF, bis(vinylenedithio)tetrathiafulvalene; *cdc*, N-cyanodithiocarbimate; *cbdt*, 4-cyanobenzene-1,2-dithiolate; Cyclam, 1,4,8,11-tetraazacyclotetradecane; Cyclem, 1,4,7,10-tetraazacyclododecane; DC18C6-B, cis-anti-cis-dicyclohexyl-18-crown-6, isomer B; DC18C6-A, cis-syn-cis-dicyclohexyl-18-crown-6, isomer A; *dmit*, 1,3-dithiol-2-thione-4,5-dithiolate; *dmio*, 1,3-dithiol-2-one-4,5-dithiolate; DMSO, dimethylsulfoxide; DPEphos, bis(2-diphenylphosphinophenyl)ether; *DazfDTs*, diazafluorene dithiolates; *dcbdt*, 4,5-dicyanobenzene-1,2-dithiolate; DMF, dimethylformamide; *dpesdt*, bis(2-pyridylethylsulfanyl)-1,2-dithiolate; *dpddt*, 5,6-dipyridyl-1,4-dithiine-2,3-dithiolate; *fendt*, 5,6-dithio-1,10-phenanthroline; H_2*dcbdt*, 4,5-dicyanobenzene-1,2-dithiol; H_2*cbdt*, 4,5-cyanobenzene-1,2-dithiol; H_2*pdt*, pyrazine-2,3-dithiol; H_2*pds*, pyrazine-2,3-diselenol; hfac, hexafluoroacetylacetonate; Hg(OAc)$_2$, mercury(II) acetate; hmp, 2-hydroxymethylpyridinate; *i-mnt*, 1,1-dicyano-2,2-ethylenedithiolate; *mnt*, cis-1,2-dicyano-1,2-ethylenedithiolate; LDA, lithium diisopropylamide; Me$_2$Benz$_2$18C6, dimethyldibenzo-18-crown-6-ether; Me$_4$cyclam, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; MnTPP, meso-tetraphenylporphinato(manganese(lll)); N18C6, naphtho-18-crown-6-ether; Na_2*dcdmp*, disodium salt 2,5-dicyano-2,3-dithiolatepyrazine; nBu$_4$N$^+$, tetrabutyl ammonium cation; *pedt*, 1-(pyridyl)-ethylene-1,2-dithiolate; Pd$_2$(dba)$_3$, tris(dibenzylideneacetone)dipalladium(0); Pd(PPh$_3$)$_4$, tetrakis(triphenylphosphine)palladium(0); PPh$_4$$^+$, tetraphenyl phosphonium cation; SMM, single-molecule magnet; *tfadt*, 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate; TTF, tetrathiafulvalene; THF, tetrahidrofuran; VDT-TTF, vinylenedithio-tetrathiafulvalene derivatives.

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0010-8545/$ – see front matter
doi:10.1016/j.ccr.2009.12.006

ARTICLE INFO

Article history:
Received 7 September 2009
Accepted 2 December 2009
Available online 11 December 2009

Keywords:
Dithiolenes
Tetrathiafulvalenes
N coordinating groups
Metal complexes
Coordination polymers

ABSTRACT

The chemistry of transition metal dithiolene complexes containing N coordinating groups and the corresponding TTF donors, is reviewed starting from the ligand synthesis to the coordination structures where these dithiolene complexes are used as bridging units. The dithiolene ligands containing N coordinating atoms present two coordination poles which can selectively bind different metals and act as bridging units in a variety of coordination architectures. The transition metal dithiolene complexes based on these N containing ligands and the corresponding TTF donors can be themselves regarded as ligands. These can be used to coordinate other metals, potentially leading to a diversity of hetero metallic coordination architectures. With the use of appropriate auxiliary ligands they can lead to discrete metal complexes. In addition they can lead to more extended polymeric structures of different dimensionality such as 1D chains, 2D layers or even 3D polymers can also be obtained.

1. Introduction

Transition metal dithiolenes have now been researched for more than four decades due to their unique properties which are increasingly relevant to fields including electrical and magnetic materials, non-linear optics, catalysis and bioinorganic chemistry [1–5].

The earliest reported dithiolenes were already based on ligands containing N atoms, thus offering a coordination ability in addition to the dithiolate group. However, it was only more recently that the coordination potential of these N atoms attached to dithiolene ligands has been explored. The large potential for achieving novel coordination structures by exploring the coordination ability of both S and N atoms has stimulated, in recent years, the preparation of several dithiolene ligands with nitrogen coordinating groups of increasing complexity. The coordination ability of these type of ligands, with two coordination poles is however still far from fully explored and well controlled.

Dithiolene ligands containing N coordinating atoms present two coordination poles which can selectively bind different metal ions and act as bridging units in coordination architectures. In fact, transition metal dithiolene complexes based on such ligands can be themselves regarded as ligands, and used to coordinate other metals, potentially leading to a diversity of hetero metallic coordination architectures. By using appropriate auxiliary ligands, both two and three metal centered coordination structures can be easily envisaged. In addition more extended polymeric structures of different dimensionality such as 1D chains, 2D layers or even 3D polymers can also be obtained (Fig. 1).

These novel architectures are interesting from the point of view of pure supramolecular chemistry and very promising for different possible applications as molecular magnetic materials. However the demonstration of the rich coordination possibilities offered by such ligands is still in its early stages.

Several reviews concerning both dithiolene complexes and substituted TTF type donors have been previously published [6–8]. This article reviews the chemistry of transition metal dithiolene complexes containing N coordinating groups and the corresponding TTF donors summarizing both the synthesis of the corresponding ligands as well as the complexes and coordination structures where they participate as bridging ligands. Due to their strong similarities, the corresponding TTF donors often obtained from the same chemical precursors are also included.

2. Syntheses of dithiolenes and ligand precursors with N coordinating groups

The first dithiolene ligands reported in the sixties already contained cyano groups, but the coordination ability of these nitrogen

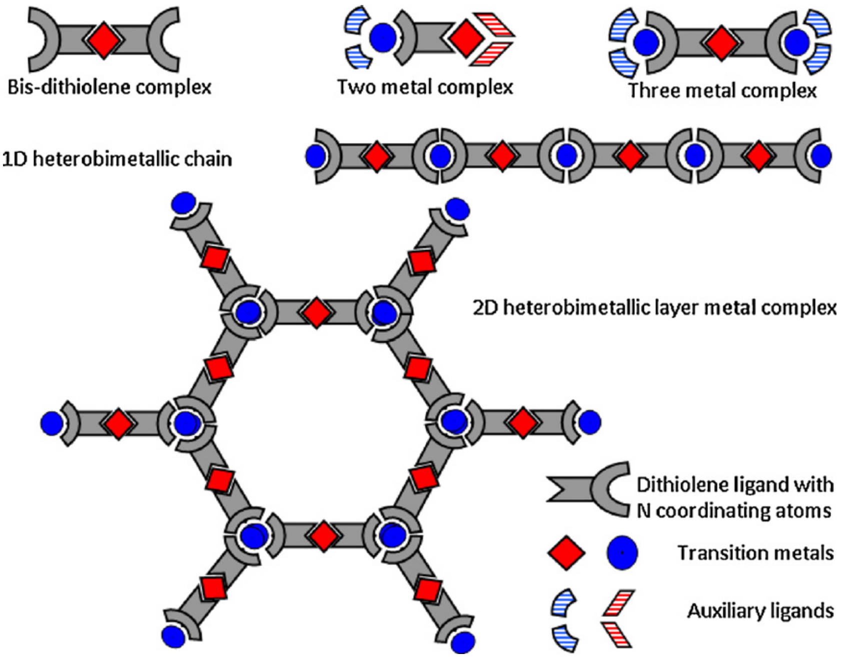


Fig. 1. Schematic representation of possible coordination structures build from dithiolene ligands with N coordinating atoms.

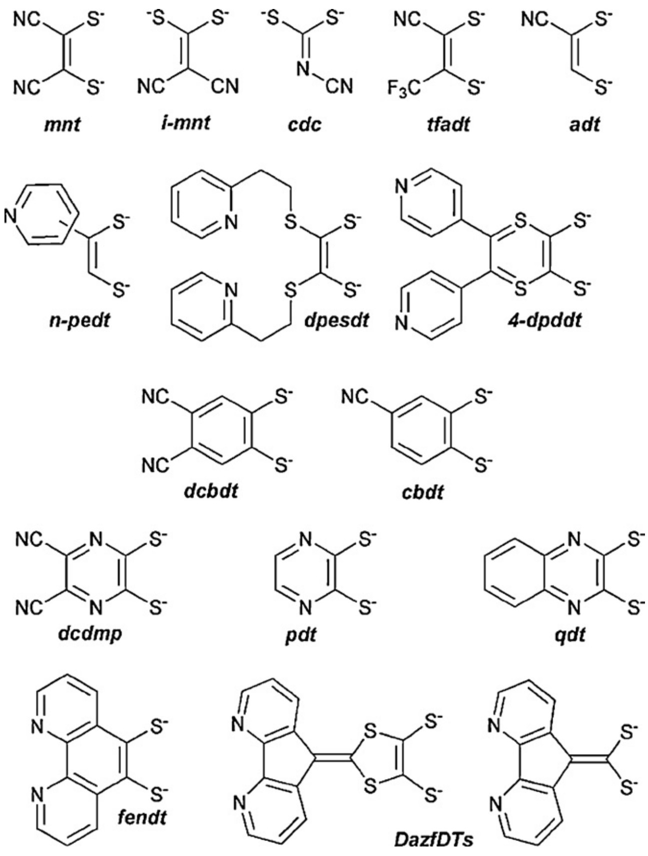


Fig. 2. Dithiolene ligands containing N coordinating atoms.

atoms was not explored at the time. From these simple ligands to the reports of more extended ligands deliberately substituted with complex N coordinating groups, as for instance, with the 1,10-phenanthroline moiety, many publications have been reported.

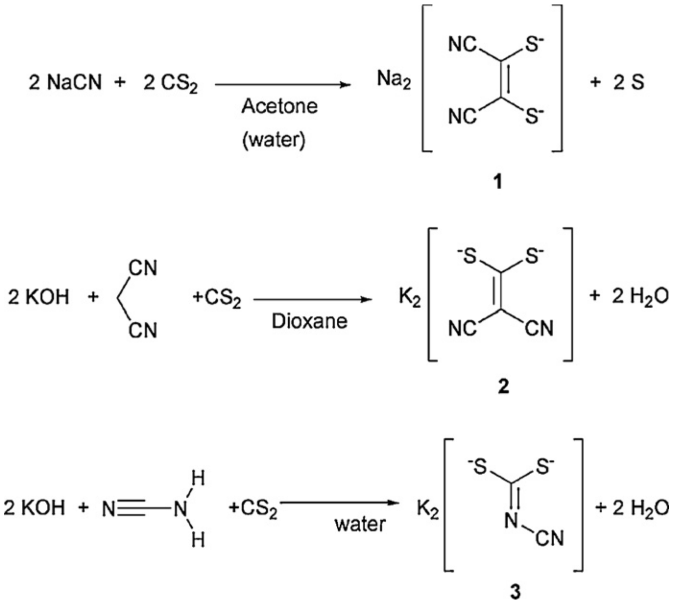
As shown in Fig. 2, presently it is possible to have small ligands with one or two N coordinating sites, where the coordinating groups are either directly linked or appended to the C_2S_2 dithiolene group. The ligands with only one coordinating group are asymmetric and the coordinating group can be either a cyano (*adt*, *tfadt*) or a pyridyl group (*n-pedt*). These asymmetric small ligands have been less explored than the symmetric ones with two cyano groups (*mnt*, *i-mnt* or *cdc*).

There are also ligands where the N coordinating group, pyridine (*dpesdt*) or pyrazine, are linked to the thiocarbonate ring by a sulphur alky chain. The sulphur alkyl chain allowed more flexibility to the N coordinating groups.

More extended and sulphur-rich ligands have also been reported with the introduction of a pyridine functionalized dithiine ring fused to the dithiolene group (*n-dpddt*). Instead of a dithiine ring it is also possible to attach a cyano functionalized benzene ring to the dithiolene group with one (*cbdt*) or two (*dcbdt*) cyano groups.

Pyrazine dithiolate derivatives cannot be left outside this section. Ligands with cyano functionalized pyrazine rings (*dcdmp*) or even without the cyano functionalization (*pdt* and *qdt*) are already know. In fact the coordination ability of pyrazine nitrogen atoms to some alkaline and copper metal ions have been already demonstrated.

The 1,10-phenanthroline ligand functionalization in the 5,6 position have been recently deserved increasing attention with the synthesis of 5,6-dithio-1,10-phenanthroline derivatives, very attractive dithiolate ligand precursor also with N coordination ability. However the bisdithiolate complexes with this ligand remain yet to be explored. More success have been achieved with a bipyridine derivative with a structure similar to the 1,10-phenanthroline, the 4,5-diazafluorene. Interesting derivatives of this unit have been reported as 1,2-dithiolate and 1,1-dithiolate precursors and corresponding bisdithiolate complexes.



Scheme 1.

2.1. Complexes based on small ligands

2.1.1. mnt, i-mnt and cdc

The *mnt*, *i-mnt* and in a smaller extent the *cdc* bisdithiolene complexes, which are among the earliest dithiolenes reported, have been widely used in molecular materials as it can be found in several general reviews on dithiolene chemistry [1,5,9]. They were also the first dithiolene ligand substituted with N coordinating groups. The ligand *mnt* (*mnt* = maleonitrile dithiolate or cis-1,2-dicyano-1,2-ethylenedithiolate) first prepared by Bahr and Schleitzer [10] in 1957 as the sodium salt (Na_2(mnt)) (**1**) (Scheme 1), through the reaction of carbon disulfide with sodium cyanide in acetone and some water.

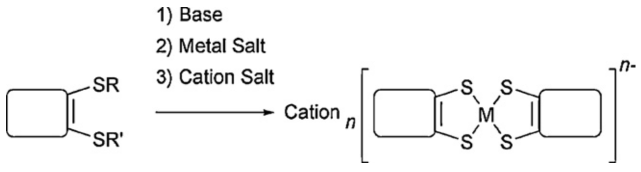
Much less explored has been the isomer *i-mnt* (*i-mnt* = 1,1-dicyano-2,2-ethylenedithiolate) initially prepared by Jensen and Henriksen [11] in 1968 as the potassium salt K_2(*i*-mnt) (**2**) (Scheme 1).

The synthesis of the asymmetric N-cyanodithiocarbimate (*cdc*), isolated as K_2(cdc) salt (**3**), was been described in the sixties by Fackler and Coucouvanis [12] (Scheme 1).

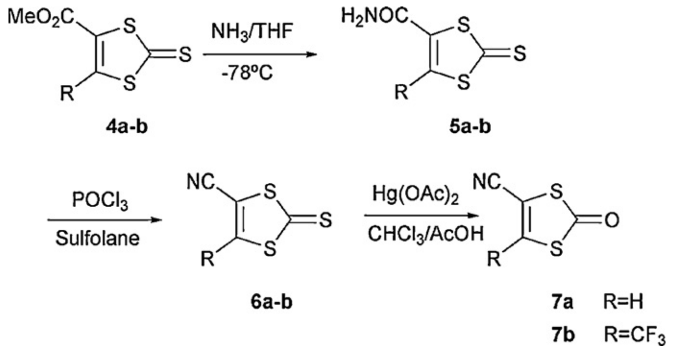
The preparation of transition metal dithiolene complexes follows in general basic standard procedures as illustrated in Scheme 2 with minor differences depending on the ligand precursor used.

2.1.2. Other asymmetrically N substituted ligands: adt, tfadt, and n-pedt

Since the earliest dithiolenes other dithiolenes ligands asymmetrically substituted with N coordinating groups have been



Scheme 2.

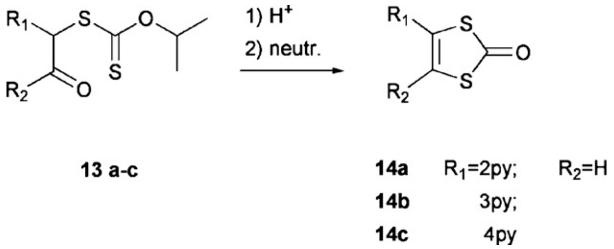


Scheme 3.

reported. More recently Fourmigue and Bertran [13] have described a new synthetic route (Scheme 3) for the asymmetrically substituted dithiolene ligand analogue to the *mnt*, the *adt* ligand (*adt* = acrylonotrile dithiolate) (**7a**). The starting ester compound (**4a**) is successively converted into the corresponding amide (**5a**) with ammonia, into the nitrile (**6a**) by $POCl_3$ dehydration and finally to the dithiocarbonate by oxymercuration. This new synthetic route avoids the use of activated Zn complexes as described by Rauchfuss and co-workers [14] or the use of cyanoacetylene in the preparation of the analogous trithiocarbonate (**6a**) previously reported by O'Connor and Jones [15]. Using the same *adt* ligand strategy another asymmetric ligand was synthesized, the *tfadt* (*tfadt* = trifluoromethyl-acrylonitrile dithiolate) (**7b**) [16].

The bis(2-cyano-1,2-ethanedithiolate)-nickelate complex $[Ni(adt)_2]^{2-/1-}$ (**8**–**9**) has been obtained by Fourmigue and Bertran in both monoanionic and dianionic oxidation states [13]. The complexes synthesis begin with the hydrolytic cleavage of corresponding dithiocarbonate with 2 equiv. of MeONa followed by addition of 0.5 equiv. $NiCl_2 \cdot 6H_2O$ and suitable cation (nBu_4N^+, PPh_4^+) yielding the air-stable dianionic diamagnetic $[Ni(adt)_2]^{2-}$ salt (**8**). The monoanionic $[Ni(adt)_2]^-$ salt (**9**), was obtained by iodine oxidation. Cyclic voltammetry shows that $[Ni(adt)_2]^{2-}$ oxidizes reversibly to the monoanionic at −0.24 V *vs* SCE while an irreversible process is observed at +0.72 V *vs* SCE (Table 1). Single crystal X-ray structures of both salts show that the nickel complexes adopt the same square-planar coordination geometry in the two different oxidation states with a *trans* configuration of the two cyano groups [13].

The synthesis of the bis(2-(trifluoromethyl)acrylonitrile-1,2-dithiolate)-nickelate $[Ni(tfadt)_2]^{2-/1-}$ (**10**–**11**) for both monoanionic and dianionic oxidation states have also been described [16]. As for the *adt* complexes the synthesis of the *tfadt* complexes follow the standard procedures. The best oxidation results to isolate the monoanionic species were achieved with ferricinium tetrafluoroborate. The dianionic bis(2-(trifluoromethyl)acrylonitrile-1,2-dithiolate)-copperate $[Cu(tfadt)_2]^{2-}$ (**12**) has been published later [17]. Cyclic voltammetry shows that **12** exhibits a reversible oxidation wave at 0.04 V *vs* SCE to the monoanionic species followed by an irreversible process with E_{ox} 1.257 V and E_{red} 0.491 V *vs* SCE (Table 1). As for the *adt* complexes, the *tfadt* complexes present a *trans* configuration of the two cyano groups.



Scheme 4.

It should be noticed that whenever possible all the presented cyclic voltametry potentials will be given *vs* SCE. Conversions were made by taking into account the solvent and supporting electrolyte [18].

The *n-pedt* = S–C(H) = C(R)–S; R = *n*-pyridyl (*n* = 2, 3 or 4) are a family of dithiolene ligands precursors with an heterocyclic N coordinating group. In these compounds a pyridine ring is directly graft to the carbon double bond following the application of the Bhattacharya and Hortmann [19] method for the synthesis of 1,3-dithiol-2-ones from the corresponding alpha-bromoketone (Scheme 4). This method involves the cyclization of the corresponding *o*-isopropyl dithiocarbonate (**13a**–**c**) in concentrated sulphuric acid affording the 1,3-dithiole-2-thione derivative (**14a**–**c**).

The first three asymmetric diamagnetic monoanionic $[Au(n\text{-}pedt)_2]^-$ (n = 2, 3, 4) complexes (**15**–**17**), were first reported by Garner and co-workers synthesized by reacting $K[AuCl_4]$ with the corresponding dithiolene, generated by basic hydrolysis of the thione-protected 1,3-dithiolate [20]. The crystal structure analysis reveals that only the monoanionic $[Au(2\text{-}pedt)_2]^-$ salt (**15**) has a cis configuration, the others present a *trans* configuration and all of them with the expected square-planar coordination geometry.

Monanionic Ni and Cu bisdithiolene complexes (**18**–**19**) based also on the 1-(pyridin-4-yl)-ethylene-1,2-dithiolate, were subsequently reported [21]. All the complexes adopt square-planar coordination geometry with a *trans* arrangement of the substituent pyridine rings. As expected the Ni monanionic complex is paramagnetic. The synthetic procedure starts with the hydrolytic cleavage of the corresponding dithiocarbonate with MeONa in MeOH and without intermediate isolation it was reacted with the selected metal salt to give an anionic complex which is precipitated as a salt in the presence of the selected cation. These complexes were obtained after recrystallisation from acetonitrile, acetone or dichloromethane/hexane. While this was expected for M = Au, for Cu and Ni even though starting from a $Ni^{II}Cl_2$ or $Cu^{II}Cl_2$ salt, the dianionic bisdithiolene complexes could not be obtained, even under nitrogen atmosphere and the monoanionic dithiolene complexes were always obtained.

The redox behaviour of the Ni complex (**18**) studied by cyclic voltammetry exhibit two quasi reversible redox waves ascribed to the couples $[Ni(4\text{-}pedt)_2]^{2-}/[Ni(4\text{-}pedt)_2]^-$ and $[Ni(4\text{-}pedt)_2]^-/[Ni(4\text{-}pedt)_2]^0$. The Cu complex (**19**) shows a cyclic voltammograms with one quasi reversible redox process ascribed to the couple $[Cu(4\text{-}pedt)_2]^{2-}/[Cu(4\text{-}pedt)_2]^-$. Scans to higher positive potentials reveal the existence of an irreversible process which should correspond to the couple $[Cu(4\text{-}pedt)_2]^-/[Cu(4\text{-}pedt)_2]^0$.

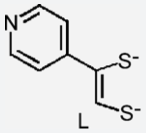
Table 1

Redox potentials *vs* SCE of $(nBu_4N)[Ni(adt)_2]$ (**9**), $(nBu_4N)[Ni(tfadt)_2]$ (**10**), $(nBu_4N)_2[Cu(tfadt)_2]$ (**12**), using [0.05 M] nBu_4NPF_6 as supporting electrolyte.

L = adt, tfadt	$[M(L)_2]^{2-}/[M(L)_2]^-$, $E_{1/2}$ [V]	$[M(L)_2]^-/[M(L)_2]^0$ [V]	Solvent	Ref.
9	−0.24	$E_{1/2} = 0.72$	CH_2Cl_2	[13,16]
10	0.01	$E_{1/2} = 0.91$	CH_2Cl_2	[16]
12[a]	0.04	$E_{ox} = 1.257 E_{red} = 0.491$	CH_2Cl_2	[17]

[a] Using [0.1 M] nBu_4NPF_6 as supporting electrolyte.

Table 2
Redox potentials *vs* SCE of $(n\mathrm{Bu_4N})[\mathrm{M}(4\text{-pedt})_2]$ M = Ni (**18**), Cu (**19**) and Au (**17**), using [0.1 M] $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte and Pt working electrode.

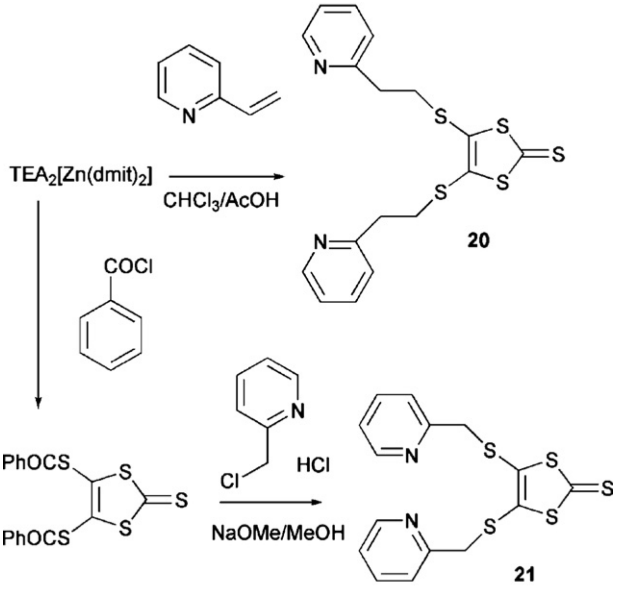
	$[\mathrm{M(L)_2}]^{2-}/[\mathrm{M(L)_2}]^{-}$, $E_{1/2}$ [V]	$[\mathrm{M(L)_2}]^{-}/[\mathrm{M(L)_2}]^{0}$, $E_{1/2}$ [V]	Solvent	Ref.
18	−0.06	0.76	CH_2Cl_2	[21]
19	0.08	1.23	CH_2Cl_2	[21]
17		1.04	CH_2Cl_2	[21]

The Au complex (**17**) exhibits one oxidation and one reduction process, assigned to the couple $[\mathrm{Au}(4\text{-pedt})_2]^{-}/[\mathrm{Au}(4\text{-pedt})_2]^{0}$ (Table 2).

In these ligands the pyridine groups, are only partially rotated relatively to the central bisdithiolene plane, thus retaining the possibility of interacting with the dithiolene π systems and therefore depending on the electron withdrawing capability can affect the redox potentials of the complexes, and the *4*-pedt complexes are easier to oxidise than those based on phenyl substituted or even unsubstituted edt ligands.

2.2. Sulphur alkyl chain dithiolenes, dpesdt

The ligands with the N coordinating groups linked to the dithiolene ring by a sulphur alky chain are a lot less explored than those where the coordinating groups are directly grafted, and only some ketone and thione ligand precursors have been reported. The attachment of alkylpyridine moities to the thiolate sulphur atoms of dmit^{2-} (4,5-disulfanyl-1,3-dithiole-2-thionate) was been reported by Becher et al. (Scheme 5) with two thiolate functionalized dmit compounds [22]. By direct reaction with 2-vinylpyridine in chloroform: acetic acid (3:1) and using the zinc salt of dmit^{2-}, $[\mathrm{Et_4N}]_2[\mathrm{Zn(dmit)_2}]$ as starting material, it was possible to obtained **20** (4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-thione, bpedmit). The compound **21** (4,5-bis(2-pyridylmethylsulfanyl)-1,3-dithiole-2-thione, bpmdmit) was prepared by a two-step synthesis, from the zinc salt of dmit^{2-} the benzoyl protected dmit was synthesized, afterward deprotected with sodium methoxide and the resulting dithiolate alkylated using picolyl chloride.



Scheme 5.

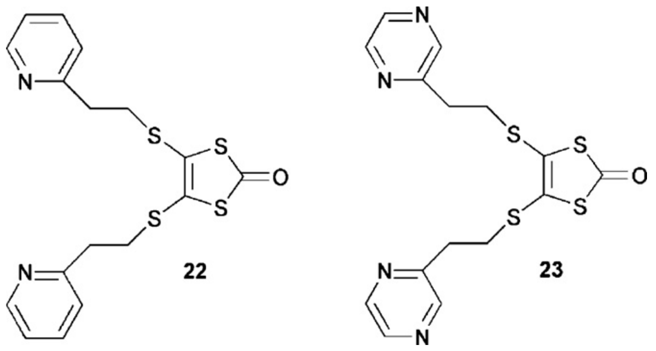
The 4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-one [23] (**22**) and 4,5-bis(2-pyrazylethylsulfanyl)-1,3-dithiole-2-one [24] (**23**) were also reported (Scheme 6). Following a similar procedure for the analogous thione, **22** was obtained from the zinc salt of dmio^{2-}. In case **23**, the starting material was the zinc salt of dmit^{2-} and the product was obtained by a two-step synthesis, initially with the synthesis of the 4,5-bis(2-pyrazylethylsulfanyl)-1,3-dithiole-2-thione followed by treatment with mercury acetate affording **23**.

The first example of a tetra-azo bisdithiolene complex was reported with the synthesis of the complex $[\mathrm{Ni(dpesdt)_2}]$ (**24**) (*dpesdt* = bis(2-pyridylethylsulfanyl)-1,2-dithiolate) by the hydrolytic cleavage of the corresponding oxo compound (**22**) with a sodium methoxide solution in the presence of *n*-$\mathrm{Bu_4NBr}$ and nickel dichloride [23]. In spite of the anaerobic preparative conditions employed and the starting Ni(II) oxidation state, the complex obtained was neutral. This corroborates with the rather low oxidation potentials revealed in the cyclic voltammetry. The redox behaviour shows two quasi reversible pairs of waves centered at −0.30 V and 1.05 V *vs* SCE, which are described to the redox couples $[\mathrm{Ni(dpesdt)_2}]^{2-}/[\mathrm{Ni(dpesdt)_2}]^{-}$ and $[\mathrm{Ni(dpesdt)_2}]^{-}/[\mathrm{Ni(dpesdt)_2}]^{0}$, respectively.

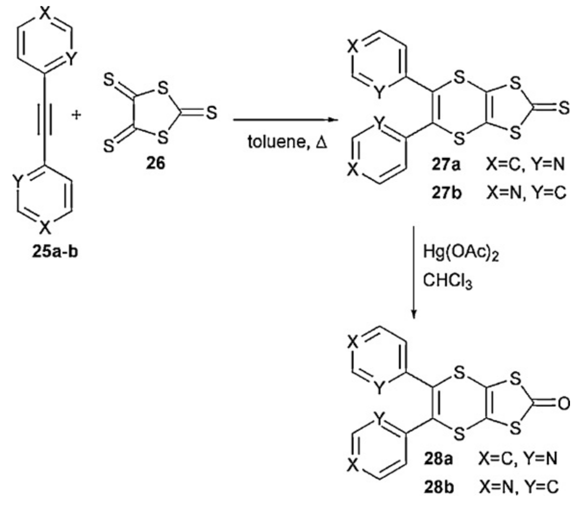
2.3. Thiine dithiolenes, n-dpddt

The introduction of a dithiine ring fused to the dithiolene group makes a sulphur-rich ligand. Pyridine functionalized dithiolene ligand precursors with dithiine ring fused to the dithiocarbonate/trithiocarbonate ring have been reported recently (*dpddt* = 5,6-dipyridyl-1,4-dithiine-2,3-dithiolate) [25]. The thiones **27a**–**b** were prepared by the reaction of 1,3-dithiole-2,4,5-trithione **26** with the correspondent dipyridylacetylene **25a**–**b**. The treatment of **27a**–**b** with mercuric acetate afforded the oxo compounds **28a**–**b** (Scheme 7).

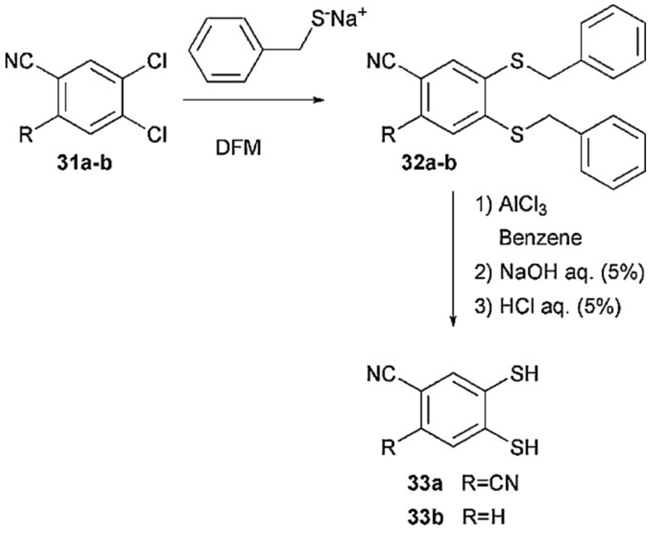
Further examples of tetra-azo bisdithiolene complexes have been recently obtained from pyridine functionalized dithiolene ligand precursors, the bis(5,6-dipyridyl-1,4-dithiine-2,3-dithiolate)-nickelate (**29**) and aurate (**30**) [25]. These are also the first examples



Scheme 6.



Scheme 7.



Scheme 8.

of bisdithiolene complexes with a unsaturated dithiine ring. They were obtained by treating the sulphur-rich pyridine functionalized dithiolene ligand (**27b**) with a freshly prepared sodium methoxide solution, and without isolating the sodium dithiolate, adding a solution of nickel(II) chloride or potassium gold(III) chloride in methanol. Both dithiolene complexes were precipitated as tetrabuthylammonium salts by the addition of a methanol solution of $n\mathrm{Bu_4NBr}$.

The X-ray diffraction reveals that the gold dithiolene complex crystallizes in the triclinic system, space group *P*-1 and it adopts almost perfect square-planar coordination geometry. The molecules flex about the S···S vector in the dithiine ring, a distortion which is very similar to those in the corresponding TTF and precursor thione. The pyridine rings present rotations relatively to the adjacent S–C═C–S plane. The supramolecular packing consists of parallel mixed chains of anions alternating with cations with the solvent molecules between the mixed chains.

The redox behaviour (Table 3) of **29** exhibits two redox processes at 0.05 V and 0.73 V *vs* SCE and a multielectron irreversible oxidation peak at higher potential (1.56 V) assigned to the formation of a cationic species. The process at 0.05 V, is reversible and it is ascribed to the couple $[\mathrm{Ni}(4\text{-dpddt})_2]^-/[\mathrm{Ni}(4\text{-dpddt})^2]$. The process at $E_{1/2} = 0.73$ V is not fully reversible and is most likely associated with a protonated pyridine species. Using platinum as working electrode no visible redox process for the couple $[\mathrm{Ni}(4\text{-dpddt})_2]^{2-}/[\mathrm{Ni}(4\text{-dpddt})_2]^-$ was observed, but experiments with a glassy carbon electrode, reveal this process to be centered at −0.74 V.

The cyclic voltammetry (CV) of the gold complex **30** displays two quasi reversible redox processes, at −0.57 and 1.1 V. This gold complex also exhibits a multielectron irreversible oxidation peak at higher potential (1.46 V). The quasi reversible redox process with $E_{1/2} = -0.57$ V is assigned to the couple $[\mathrm{Au}(4\text{-dpddt})_2]^{2-}/[\mathrm{Au}(4\text{-dpddt})_2]^-$ and the redox process observed at 1.1 V is ascribed to the couple $[\mathrm{Au}(4\text{-dpddt})_2]^-/[\mathrm{Au}(4\text{-dpddt})_2]$. These potentials are somewhat different from those previously found in the unsubstituted and saturated analogue $[\mathrm{Au(dddt)_2}]$. This difference can be only partially due to different experimental conditions and most likely reflect the influence of the fully unsaturated dithiine ring.

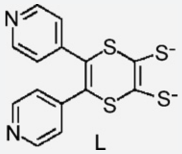
2.4. Benzene dithiolate derivatives: dcbdt, cbdt

It is also possible to fuse a benzene ring to the $\mathrm{C_2S_2}$ dithiolene group and among other substituted bezeneditiolate ligands, those with one and two cyano groups have been described and will be considered in this section. The symmetrically substituted dithiolene ligand precursor H_2dcbdt = 4,5-dicyanobenzene-1,2-dithiol (**33a**) was first described and several [M(*dcbdt*)$_2$] complexes have been reported. More recently the synthesis of the asymmetric ligand H_2cbdt = 4,5-cyanobenzene-1,2-dithiol (**33b**) was also reported [26,27]. The key compounds for the synthesis of these dithiolene ligand precursors are 4,5-dichloro-1,2-dicyanobenzene (**31a**) and 4,5-dichloro-cyanobenzene (**31b**), both commercially available (Scheme 8). The followed synthetic procedure involves the preparation of the aromatic dibenzyl sulfide (**32a**–**b**) followed by a mild cleavage with the assistance of anhydrous aluminium chloride (Scheme 8) to obtain **33a**–**b**.

With this extended π-ligand 4,5-dicyanobenzene-1,2-dithiolate, (*dcbdt*) (corresponding to thiol **33a**) complexes of different transition metal were obtained as tetrabuthylammonium salts $[(n\mathrm{Bu_4N})_z[\mathrm{M}(\mathrm{dcbdt})_2]]$ in different oxidation states. The extended nature of this ligand stabilises a diversity of oxidation states (z = 1, 2), including partially oxidized states (z = 0.4) for M = Ni, Cu and Au

Table 3

Redox potentials *vs* SCE of $(n\mathrm{Bu_4N})[\mathrm{M}(4\text{-dpddt})_2]$ M = Ni (**29**), Au (**30**), using [0.1 M] $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte and Pt working electrode, scan rate 100 mV s^{-1}.

 L	$[\mathrm{M(L)_2}]^{2-}/[\mathrm{M(L)_2}]^-$, $E^1_{1/2}$ [V]	$[\mathrm{M(L)_2}]^-/[\mathrm{M(L)_2}]^0$, $E^2_{1/2}$ [V]	Solvent	Ref.
29	−0.74[a]	−0.05/−0.06[a]	$\mathrm{CH_2Cl_2}$	[25]
30	−0.57	1.1	$\mathrm{CH_2Cl_2}$	[25]

[a] Glassy carbon as working electrode.

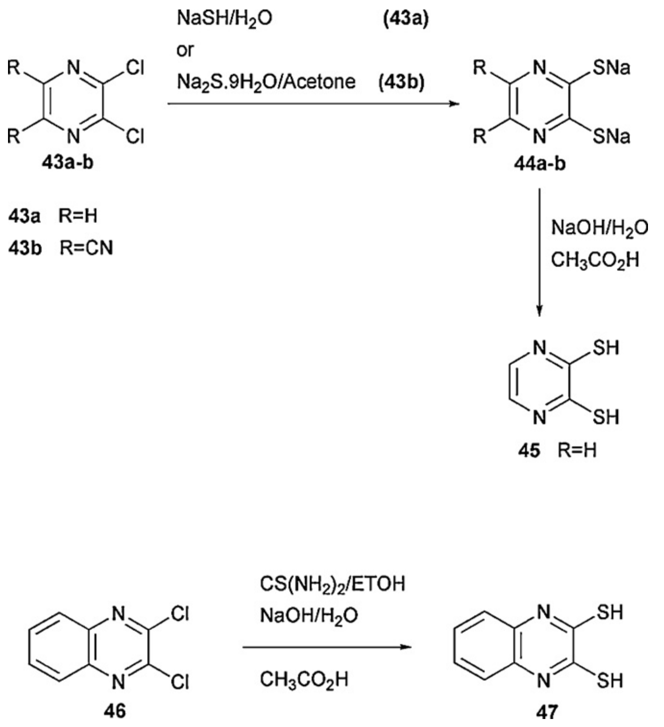
which were found to be associated with high conductivity in the solid state [26,28–30] and even metallic properties under pressure [31].

With this ligand **33a** different salts of nickel complexes were obtained; the dianionic salt $(n\mathrm{Bu_4N})_2[\mathrm{Ni(dcbdt)_2}]$ (**40**), the monanionic dimerized salt $(n\mathrm{Bu_4N})_2[\mathrm{Ni(dcbdt)_2}]_2$, and the partially oxidized Ni salt (between monoanionic and neutral) $(n\mathrm{Bu_4N})_2[\mathrm{Ni(dcbdt)_2}]_5$ (*dcbdt* = 4,5-dicyanobenzene-1,2-dithiolate) [26]. The monoanionic nickel was obtained following a standard procedure by the reaction of the dithiolate with nickel chloride, in an aqueous/alcoholic solvent mixture, and precipitated in the form of the tetrabutylammonium salt (**40**). This complex was oxidized to the monoanionic complex with iodine in acetone solution and further electrochemical oxidation led to the partially oxidized (mixed monoanionic/neutral complex) compound $(n\mathrm{Bu_4N})_2[\mathrm{Ni(dcbdt)_2}]_5$ (**39**). The monoanionic Ni complex presents a square-planar coordination geometry and is paramagnetic, while in the diamagnetic Ni complex the $\mathrm{Ni(dcbdt)_2}$ units are strongly dimerized with the metal atom in a square-pyramidal coordination geometry.

The iron complex was obtained as $(n\text{-}\mathrm{Bu_4N})_2[\mathrm{Fe(dcbdt)_2}]_2$ (**39**) in a similar way, the main difference from the other metals previously described being that the monoanionic Fe complex is obtained directly using Fe(III) salt. If an Fe(II) salt were used the monoanionic Fe complex would be obtained simply by air oxidation [32]. The same procedure enables the preparation of the complexes with different metals (M = Au, Co, Cu, Pd, Pt, Zn) [28]. The oxidation state of the resulting complexes depends on the starting metal salt, the reaction conditions and the redox stability of the final product. The dianionic complexes were obtained from $\mathrm{MCl_2}$ salts (M = Co, Cu, Pd, Pt, Zn), and recrystalized from acetone. With exception of Pd and Zn, the monoanionic complexes could be obtained by oxidation of the corresponding dianions with iodine in acetone solution. The monoanionic complexes could be obtained directly after complexation for M = Au from the $\mathrm{KAuCl_4}$ salt and also, as described previously, for iron from $\mathrm{FeCl_3}$. For cobalt, the monoanionic complex $[\mathrm{Co(dcbdt)_2}]^-$ could also be obtained directly, starting from $\mathrm{CoCl_2}$ and with oxidation by prolonged air exposure.

At lower potentials it is possible to observed a redox process assigned to the couple $[\mathrm{M(dcbdt)_2}]^{2-}/[\mathrm{M(dcbdt)_2}]^-$ for almost all complexes. This process is reversible for Co, Cu, Ni and Pd complexes, and is quasi reversible for the Pt complex (Table 4). For Au and Fe complexes a single irreversible reduction wave is observed.

The synthesis of the related dithiol precursor of the monosubstituted ligand **33b** (4-cyanobenzene-1,2-dithiolate (cbdt)) (Scheme 8) was recently reported enabling the preparation of the iron complex as $(n\mathrm{Bu_4N})[\mathrm{Fe(cbdt)_2}]$ (**42**) which so far is the only complex described with this ligand [27]. This complex was obtained by the same synthetic procedure used in the synthesis of the dcbdt analogue. The crystal structure consists in cis $[\mathrm{Fe(cbdt)_2}]^-$ dimers in a trans fashion, with Fe in the usual square-pyramidal coordination geometry, the dimmers being well isolated from each other by the cations. The magnetic susceptibility shows that the $[\mathrm{Fe(cbdt)_2}]^-$ units have a $S = 3/2$ spin configuration.



Scheme 9.

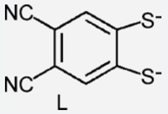
The cyclic voltammetry behaviour of **42** in dichloromethane solutions with $(n\text{-}\mathrm{Bu_4N})\mathrm{PF_6}$ as supporting electrolyte showed that this compound is stable in the range −0.14 to 0.86 V *vs* SCE. Complex irreversible oxidation reduction processes occur at these limits denoting a possible equilibrium between dimerized and dissociated $[\mathrm{Fe(cbdt)_2}]$ species in solution.

2.5. Pyrazine dithiolate derivatives: pdt, qdt, dcdmp

With the introduction of a pyrazine ring fused to the dithiolene group, further families of dithiolene ligands precursors were obtained. Three pyrazine functionalized dithiolene ligand precursors have been reported, all being prepared from the commercially available dichlorides **43a–b** and **46** (Scheme 9). The smaller and simpler one, pyrazine-2,3-dithiol (*H_2pdt*) (**45**), can be prepared

Table 4

Redox potentials *vs* SCE of $(n\mathrm{Bu_4N})_2[\mathrm{M(dcbdt)_2}]$ M = Pt (**34**), Pd (**35**), Cu (**36**), Co (**37**), Au (**38**), Fe (**39**), Ni (**40**) and Zn (**41**), using [0.1 M] $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte and Pt as working electrode.

 L	$[\mathrm{M(L)_2}]^{2-}/[\mathrm{M(L)_2}]^-$	$[\mathrm{M(L)_2}]^-/[\mathrm{M(L)_2}]_5{}^{2-}$		Solvent	Ref.
	$E_{1/2}$ [V]	E^1 [V]	E^2 [V]		
34	0.42	1.16	1.50	$\mathrm{CH_3CN}$	[28]
35	0.72	1.16	1.38	$\mathrm{CH_3CN}$	[28]
36	0.29	1.36	1.47	$\mathrm{CH_3CN}$	[28]
37	0.15	1.28	1.35	$\mathrm{CH_3CN}$	[28]
38	−0.97	1.17	1.56	$\mathrm{CH_3CN}$	[28]
39	0.08	1.25	1.43	$\mathrm{CH_3CN}$	[32]
40	0.44	1.31	1.59	$\mathrm{CH_3CN}$	[26]
41		1.25	1.63	$\mathrm{CH_3CN}$	[28]

from pyrazine-2,3-dichloro (**43a**) [33]. The dicyano pyrazine functionalized dithiolate ligand precursor was obtained as a, disodium salt 2,5-dicyano-2,3-dithiolatepyrazine (*Na_2dcdmp*) (**44b**), from 2,5-dicyano-2,3-dichloro (**43b**). The precursor for the unsubstituted *qdt* ligand was a thiol, quinoxaline-2,3-dithiol (*H_2qdt*) (**47**) which can be prepared from the quinoxaline-2,3-dichloride (**46**) [34].

The transition metal complexes with the *pdt* ligand reported so far are restricted to $Na[Cu(pdt)_2]{\cdot}2H_2O$ (**48**) and nBu$_4$N[Cu(pdt)$_2$]·(**49**) [35]. It is worth mention that the ligand analogous to *pdt* but with selenium, *pds*, has been prepared following a similar procedure [33,36] and a much larger number of metal complexes and salts with this ligand, such as $Li[Cu(pds)_2]{\cdot}3H_2O$ (**50**), $Na[Cu(pds)_2]{\cdot}2H_2O$ (**51**), nBu$_4$N[Cu(pds)$_2$] (**52**), [Cu(pds)$_2$]Cu (**53**), nBu$_4$N[Au(pds)$_2$] (**54**), (nBu$_4$N)$_2$[Ni(pds)$_2$] (**55**), $Na_2[Ni(pds)_2]{\cdot}2H_2O$ (**56**), $Na_2[Ni(pds)_2]_2{\cdot}4H_2O$ (**57**) [35,37–39]. TTF$_2$ [Au(pds)$_2$]$_2$ (**58**) TTF$_3$ [Au(pds)$_2$]$_2$ (**59**) and TTF$_3$ [Au(pds)$_2$]$_3$ (**60**) have been reported [40]. These selenium compounds are not described in detail because they may be considered marginal to the scope of the present review which focus mainly on dithiolenes.

With the *dcdmp* ligand several complexes, [M(dcdmp)$_2$], of different transition metals M = Ni, Pd, Au, Cu and some charge transfer salts of these complexes with different donors have been reported [41–45]. The Au complex was obtained as the diamagnetic salt nBu$_4$N [Au(dcdmp)$_2$] (**61**) and its cyclic voltammetry shows a pair of symmetric reversible redox waves at −0.269 V *vs* SCE ascribed to the pair $Au(dcdmp)_2{}^{2-}/Au(dcdmp)_2{}^{-}$ [43]. The copper complex was obtained as dianionic paramagnetic complex in (nBu$_4$N)$_2$[Cu(dcdmp)$_2$] (**62**) and its cyclic voltammetry also shows a pair of symmetric reversible redox waves, 0.566 V *vs* SCE ascribed to the pair $Cu(dcdmp)_2{}^{2-}/Cu(dcdmp)_2{}^{-}$ [44]. These complexes have been also combined with ET and TTF donors to obtain a few charge transfer salts aiming at obtaining conducting materials [42,45].

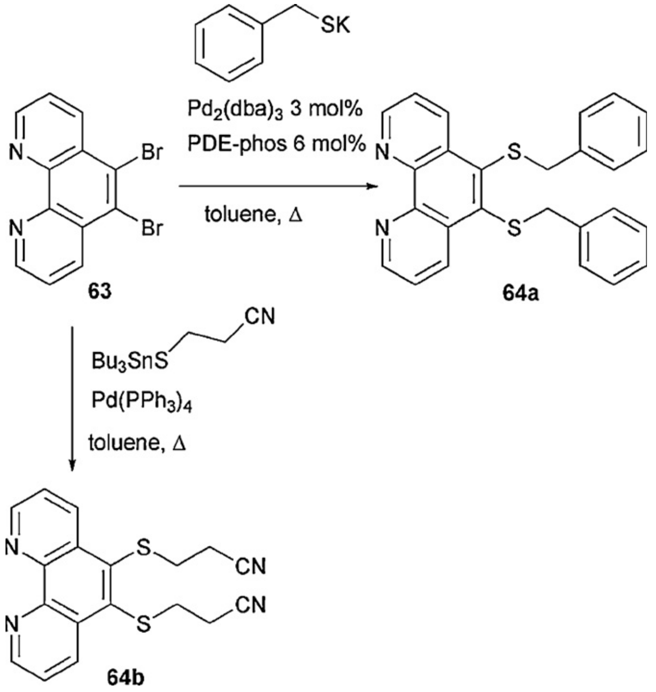
With the *qdt* ligand a large number of bis(quinoxaline-2,3-dithiolate) complexes, M(qdt)$_2$ with different transition metals M = Zn, Cu, Ni, Pd, Pt, Co, Fe and Au have been studied since late sixties of the last century [34,46–52]. These complexes can be easily protonated changing colour and some of them were used as counterions of charge transfer salts with donors commonly employed in the preparation of conducting materials [53,54].

2.6. Phenanthroline–dithiolate ligands

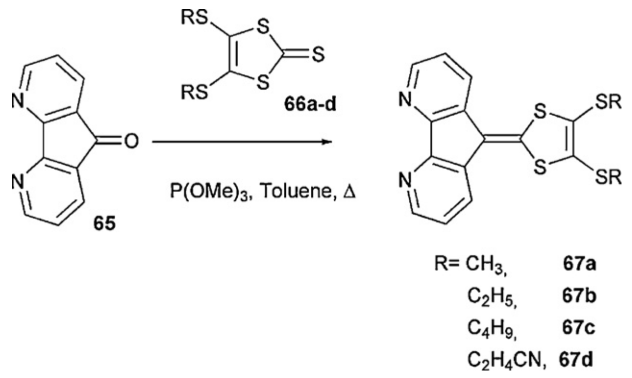
The functionalization of 1,10-phenanthroline in the 5 and 6 positions allowed the synthesis of 5,6-dithio-1,10-phenanthroline derivatives; a very attractive dithiolate ligand due to the combination of dithiolene and phenanthroline coordination ability. Recently, two 5,6-dithio-1,10-phenanthroline derivatives (**64a–b**) have been described (Scheme 10). Both were obtained via a palladium catalyzed cross-coupling reaction using **63** as starting compound. The compound **64a** was obtained by the cross-coupling with benzylthiol in the presence of a base, and using $Pd_2(dba)_3$/DPEphos as a catalyst [55]. The compound **64b** was synthesized by the cross-coupling reaction with 3-(tributylstannylsulfanyl)propanenitrile in the presence of $Pd(PPh_3)_4$ [56]. Both routes lead to two 5,6-dithio-1,10-phenanthroline derivatives that can be used as dithiolene ligand precursors. However, dithiolene complexes with the 5,6-dithio-1,10-phenanthroline ligand have not been reported yet.

2.7. Diazafluorene dithiolates, DazfDTs

4,5-Diazafluorene is a 2,2′-bipyridine derivative with a structure similar to 1,10-phenanthroline. Ligands based on this unit have been reported either as 1,2-dithiolate or as 1,1-dithiolate precursors. Originally, Sato et al. [57] (**67a–c**) and later Baudron and Hosseini [58] (**67d**) described the synthesis of new 1,2-dithiolene ligand precursors with 4,5-diazafluorene moiety, by trimethyl phosphite coupling of **65** with **66a–d** (Scheme 11).

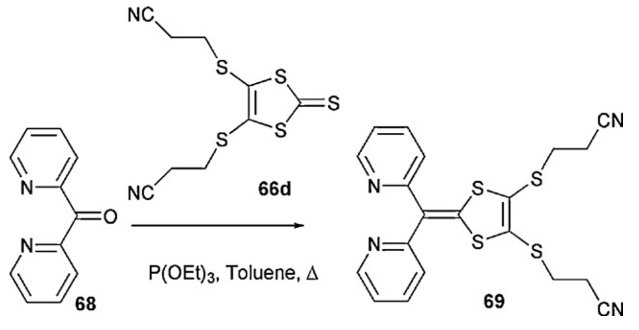


Scheme 10.

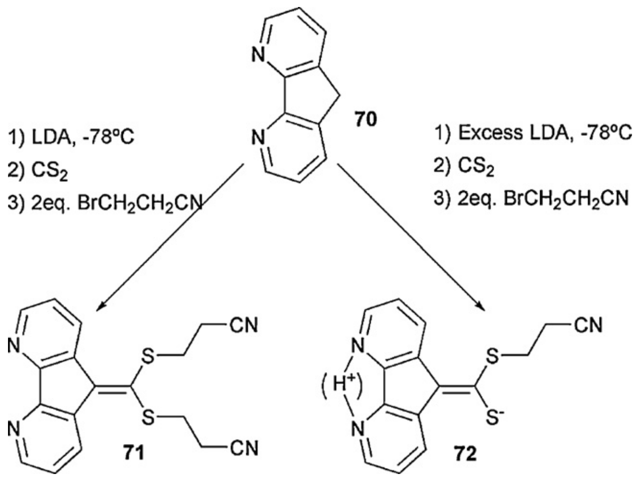


Scheme 11.

In a similar way it was possible to attach two pyridine units to a 1,2-dithiolene group affording a ligand similar to the 4,5-diazafluorene. Liu et al. [59] obtained the ligand **69** by a cross-coupling method in the presence of $P(OEt)_3$ (Scheme 12). However



Scheme 12.



Scheme 13.

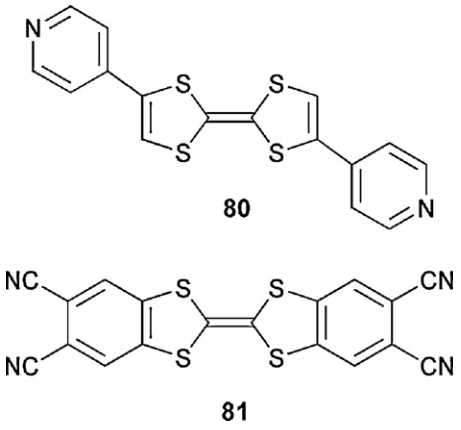
until now no bisdithiolene complexes with this ligand have been reported.

Recently, other 1,1-dithiolene ligands have been explored, namely those with a 4,5-diazafluorene moiety as N coordinating group. Baudron et al. [60,61] reported the lithiation of **70** by LDA (lithium diisopropylamide), and its subsequent reaction with CS_2 followed by treatment with 3-bromopropionotrile, depending on the stoichiometric or excess use of LDA, afforded compounds **71** or **72**, respectively (Scheme 13).

1,1-Dithiolene ligand precursors (**71** or **72**) with 4,5-diazafluorene allowed Baudron to prepared a series of dianionic discrete dithiolene metal complexes either with square-planar (Ni(**73**), Cu(**74**) and Pd(**75**)) or distorted tetrahedral (Zn(**76**) and Hg(**77**)) coordination geometry [60,61]. The paramagnetic Cu dianionic complex (**74**) could not be isolated in large quantities. For compounds **73**, **75**, **76** and **77**, two irreversible oxidation processes could be observed. Where two reduction processes are present for **77** only one process was detected at variance with the others three complexes (Table 5).

The Ni, Pd and Hg units are still rare cases of complexes that have been successfully used for the sequential formation of molecular architectures of higher complexity including hetero trinuclear complex and coordination polymers.

With the 4,5-diazafluorene unit, using the 1,2-dithiolene ligand precursor **67d** were synthesized dianionic discrete Ni (**78**) and Hg (**79**) complexes [58]. The redox behaviour of complex **78** studied by cyclic voltammetry shows one reduction (−1.805 V *vs* SCE) and two oxidation processes (−0.231 and 0.072 V *vs* SCE). The reduction process seems to be ligand-centered. The complex **79** displays two close and irreversible oxidation waves at −0.40 and 0.47 V as well as one irreversible reduction wave at −1.07 *vs* SCE (Table 5).



80

81

Scheme 14.

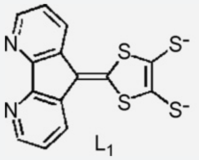
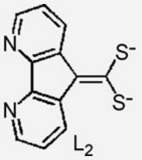
3. TTF derivatives

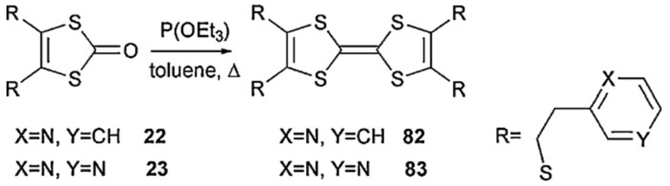
As there are already several extensive reviews on substituted tetrathiafulvalene compounds [6–8], in this section we will focus our attention on a few cases of TTF donors substituted with N coordinating groups, which correspond or are related to the dithiolene complexes above discussed. These TTF donors (**80**, **82**, **85**) are the organic analogues of the dithiolene complexes [M(*4*-pedt)$_2$], [M(dpedt)$_2$] and [M(*4*-dpddt)$_2$], respectively. The compound, **80** acting as a ligand, enabled the synthesis of a binuclear iridium complex [62–64]. It should be referred here also a less explored TTF type donor, tetracyanodibezotetrathiafulvalene (TCN-DBTTF) (**81**) corresponding to the M(dcbdt)$_2$ complexes described in Section 2.4, which so far has lead only to one salt [65] (Scheme 14).

3.1. 4,4′,5,5′-Tetrakis(2-pyridylethylsulfanyl) tetrathiafulvalene and 4,4′,5,5′-tetrakis(2-pyrazylethylsulfanyl) tetrathiafulvalene

The TTF derivatives 4,4′,5,5′-tetrakis(2-pyridylethylsulfanyl) tetrathiafulvalene (**82**) and 4,4′,5,5′-tetrakis(2-pyrazylethylsulfanyl) tetrathiafulvalene (**83**) were obtained from the phosphite-mediated homo-coupling represented in Scheme 15 [24]. Both TTFs are electroactive ligands and exhibit the two reversible oxidation waves typical of TTF derivatives. While for **83** these waves are clearly reversible, slightly larger separations between anodic and cathodic peaks are observed in **82**. Compared to BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene), the attachment of the pyridine and pyrazine units mainly increases the first redox wave

Table 5
Redox potentials *vs* SCE of $(Et_4N)_2[Ni(L_2)_2]$ M = Ni (**73**), Pd (**75**), Zn (**76**), Hg (**77**) and of $(nBu_4N)_2[Ni(L_1)_2]$ M = Ni (**78**) and Hg (**79**), using [0.1 M] nBu_4NPF_6 as supporting electrolyte, scan rate 100 mV s^{-1}.

 L$_1$  L$_2$	$E^1_{1/2}$ [V]	$E^2_{1/2}$ [V]	$E^3_{1/2}$ [V]	$E^4_{1/2}$ [V]	Solvent	Ref.
73	0.37	0.14	−0.05	−0.79	DMF	[61]
75	0.77	0.22	−0.81	−1.55	DMF	[61]
76	0.48	0.37	−0.73	−1.52	DMF	[61]
77	0.47	0.40	−1.09		DMF	[61]
78	0.072	−0.231	−1.805		DMF	[58]
79	0.47	0.40	−1.07		DMF	[58]



Scheme 15.

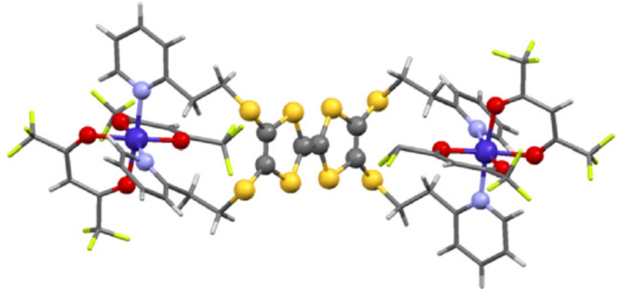
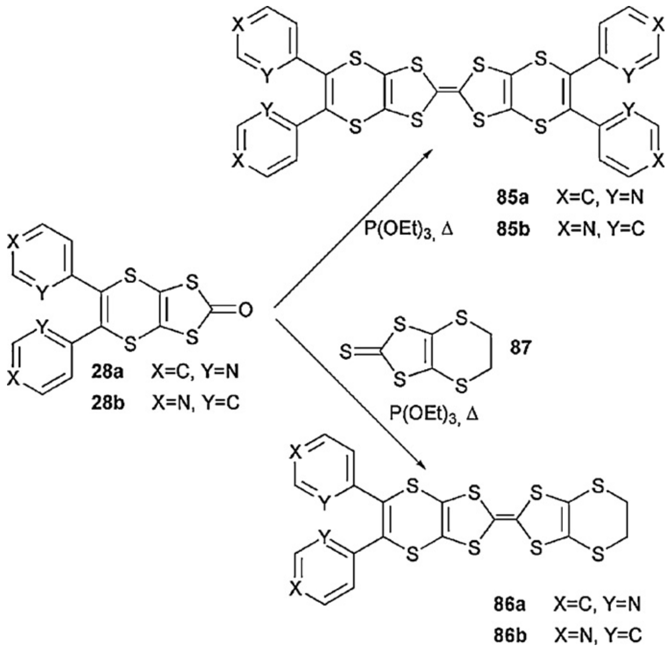


Fig. 3. Molecular structure of the dinuclear Co^{II}-coordination complex **84**.

potential due to the electron-withdrawing effect of the pyridine and pyrazine units (Table 6). Single crystal X-ray diffraction analyses of **82** and **83** show in their structures a strong segregation of TTF and N coordinating groups [24].

The pyridine-substituted donor **82** was used as a bridging ligand to prepare a dinuclear Co^{II}-coordination complex [**82**$Co_2(hfac)_4$] (hfac = hexafluoroacetylacetonate) obtained by treatment of the electron donor **82** with [$Co(hfac)_2$] (Fig. 3). This coordination to the Co^{II} ions does not significantly change the redox potentials of the donor. The dinuclear complex (**84**) presents an effective magnetic moment of ca. 8 μB, corresponding to nearly independent $S = 3/2$ spins with weak antiferromagnetic interactions below 65 K.

3.2. Pyridine functionalized (vinylenedithio)tetrathiafulvalene (VDT-TTF) derivatives



Scheme 16.

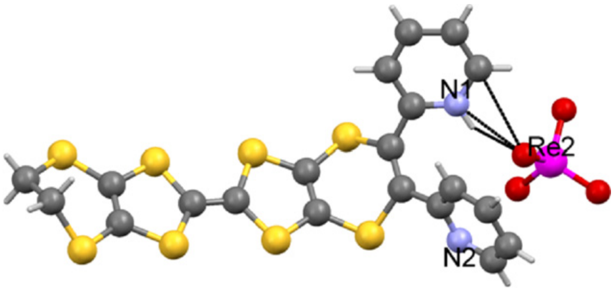


Fig. 4. Molecular structure of charge transfer salt **88**.

The homo-coupling of **28a** or **28b** in triethyl phosphite afforded the tetra(pyridyl)-bis(vinylenedithio)-TTF derivatives **85a** or **85b** (Scheme 16). Cross-coupling of the oxo compounds **28a** or **28b** with the unsubstituted thione **87** in triethyl phosphite gave the dipyridyl donors **86a** and **86b** (Scheme 16). Cyclic voltammetry (Table 7) of the donor **85b**, **85b** shows a pair of quasi reversible redox waves centred at 1.17 V *vs* SCE, similar to the parent unsubstituted BVDT-TTF (bis(vinylenedithio)tetrathiafulvalene) [66] that shows a similar process at 1.15 V *vs* SCE. All the other donors show two pairs of reversible single-electron redox waves typical of the TTF system. These values are higher when compared with those of the related BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) [67] donor ($E^1_{1/2} = 0.85$ V, $E^2_{1/2} = 1.25$ V *vs* SCE). The first oxidation potentials are similar to that of BVDT-TTF apart from donor **86a**, which is ca. 0.1 V lower. The pyridyl substitution does not significantly change the redox potentials of these donors. The ability of these donors to prepare new cation radical salts have been already demonstrated by a dicationic salt of donor **86a** with perrhenate (**88**) obtained by electrocrystallisation in which the donor is both protonated and oxidized (Fig. 4).

Table 6
Redox potentials *vs* SCE, using [0.1 M] nBu$_4$NPF$_6$ as supporting electrolyte and Pt working electrode, scan rate 100 mV s^{-1}.

	$E^1_{1/2}$	$E^2_{1/2}$	Solv. ref. electr.	Ref.
83	0.92	1.25	CH_2Cl_2	[24]
	0.92	1.1	THF	[24]
83	0.96	1.26	CH_2Cl_2	[24]
84	0.97	1.16	THF	[24]

Table 7
Redox potentials *vs* SCE, using [0.1 M] nBu$_4$NPF$_6$ as supporting electrolyte and Pt working electrode, scan rate 100 mV s^{-1}.

	$E^1_{1/2}$	$E^2_{1/2}$	Solvent	Ref.
85a	1.13	1.48	CH_2Cl_2	[25]
85b	1.17		CH_2Cl_2	[25]
86a	1.05	1.44	CH_2Cl_2	[25]
86b	1.11	1.43	CH_2Cl_2	[25]

4. Dithiolene molecular architectures; from discrete metal complexes to coordination polymers

4.1. Small structural units: i-mnt, mnt, adt, tfadt, 4-pedt

Bisdithiolene nitrile containing complexes have, since their first synthesis wide application as the basis of conducting or magnetic molecular materials. More recently their coordination ability through the N atoms has also been explored, but only to a limited extent particularly when involving magnetic ions. The majority of the reported compounds involving coordination through the nitrile groups, and in the particular case of *i-mnt* bisdithiolene complexes,

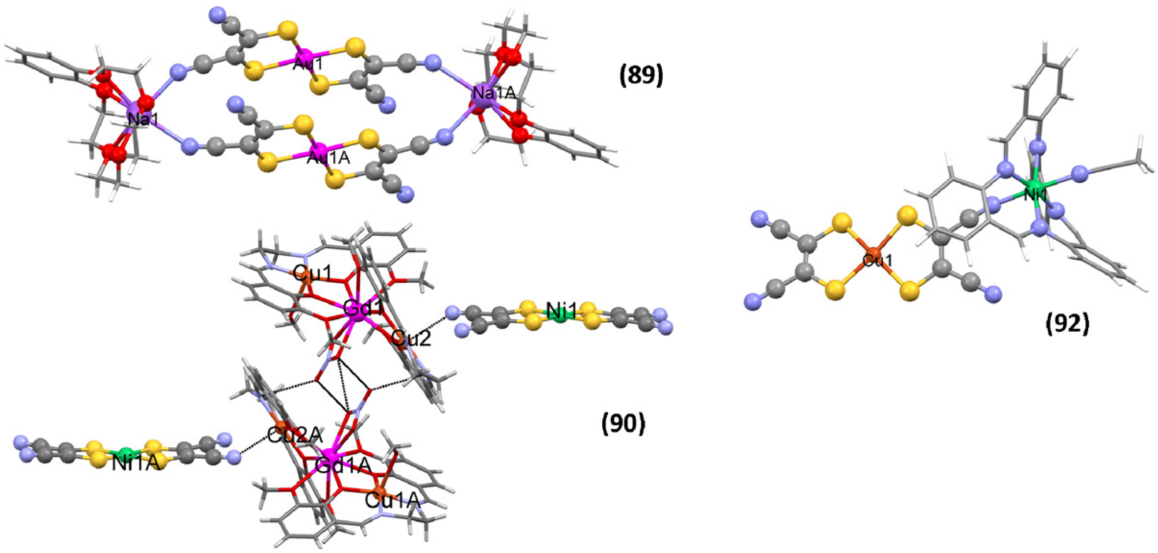


Fig. 5. Molecular structure of a heterodimeric (**89**–**90**) and a heterobinuclear (**92**) complexes, solvent molecules where omitted.

are limited to Na$^+$ and K$^+$ cations combined with diamagnetic dianionic bisdithiolene complexes. With the *mnt*, *adt*, *tfadt* and *4-pedt* bisdithiolene complexes there are already some compounds involving paramagnetic metal ions.

In the following we present the main coordination architectures obtained by the double coordination ability of these ligands. All these architectures fulfil the basic requirements of charge neutralization and completeness of the metals coordination sphere, often achieved by macrocyclic ligands.

4.1.1. Heteronuclear complexes

Heterodimeric complexes—A heterodimeric complex, [Na(B15C5)][Au(mnt)$_2$]·$C_2H_4Cl_2$ (**89**), was obtained. Two [Au(mnt)$_2$]$^-$ monoanionic complexes as bridging ligands between two [Na(B15C5)]$^+$ complex cations, forming a dimeric structure bridged via Na–N interactions (Fig. 5, left) [68].

In the heterodimeric complex, [{(CH$_3$OH)CuL^2}{CuL^2}Gd(O$_2$NO){Ni(mnt)$_2$}][Ni(mnt)$_2$]·CH$_2$Cl$_2$ (**90**), L^2 = N,N′-ethylene-di(3-methoxysalicylideneiminato), the monoanionic [Ni(mnt)$_2$]$^-$ units are stacked as tetramers. One of the [Ni(mnt)$_2$]$^-$ units is coordinated to one of the Cu centers of the trinuclear [Cu$_2$Gd] unit through one nitrile group, and the other is discrete. In this compound the [Cu$_2$Gd] units dimerize by two nitrato groups, acting as a bridge that chelates a gadolinium ion from one unit and the Cu ion from the other unit (Fig. 5, left). The tetramer unit [{(CH$_3$OH)CuL^2}{CuL^2}Gd(O$_2$NO) {Ni(mnt)$_2$}]$_2$$^{2+}$ is dicationic, and the discrete [Ni(mnt)$_2$]$^-$ units assure the charge compensation. Ferromagnetic exchange interactions within the trinuclear [Cu$_2$Gd] motifs occurs, however the [Ni(mnt)$_2$]$^-$ units are strongly antiferromagnetically coupled at low temperature and their contribution to the global magnetism is visible even in the high-temperature regime [69].

[{Mn^{II}$_2$Mn^{III}$_2$(hmp)$_6$(CH$_3$CN)$_2$}{Pt(mnt)$_2$}$_4$][Pt(mnt)$_2$]$_2$ (**91**), (hmp = 2-hydroxymethylpyridinate) cannot be considered exactly an heterodimeric complex, and it is a coordination polymeric material based on Mn$_4$ single-molecule magnet (SMM) clusters and a bisdithiolene complex. This compound comprises six [Pt(mnt)$_2$]$^{n-}$ units in addition to a common Mn^{II}$_2$Mn^{III}$_2$ double-cuboidal unit, [Mn^{II}$_2$–Mn^{III}$_2$(hmp)$_6$(CH$_3$CN)$_2$]$^{4+}$ = ([Mn$_4$]$^{4+}$). Four of the six [Pt(mnt)$_2$]$^{n-}$ units, are coordinated to the [Mn$_4$]$^{4+}$ unit, forming a discrete subunit of [[Pt(mnt)$_2$]$_2$$^-$[Mn$_4$]–[Pt(mnt)$_2$]$_2$]. This compound was the first example of a hybridized material exhibiting simultaneously SMM behaviour at low temperatures, with a ground state total spin $S_T = 9$ and reasonable electronic conductivity 0.22 S/cm at room temperature, although with a semiconducting behaviour and an activation energy of 136 meV [70].

Heterobinuclear complex—An isolated example of a discrete hetrobinuclear with a dithiolene ligands is given by [(CH$_3$CN)Ni(L)][Cu(mnt)$_2$]·CH$_3$CN (**92**) *L* = tetrabenzo[b,f,j,n][1,5,9,13] tetra-azacyclohexadecine. This involves one [Cu(mnt)$_2$]$^{2-}$ dianionic complex and one [Ni(L)]$^{2+}$ dicationic complex, linked to via Ni–N interactions (Fig. 5, right). Both copper(II) and nickel(II) metal centers are paramagnetic, but they

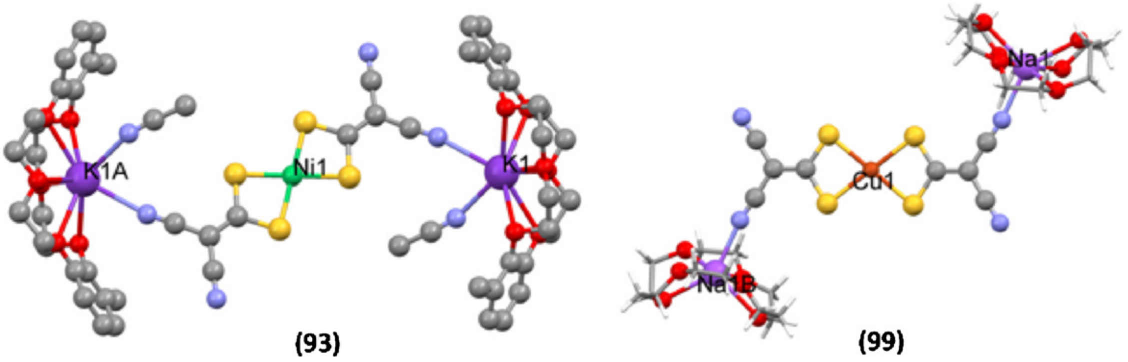


Fig. 6. Molecular structure of trinuclear complexes: a diamagnetic (**93**) and a paramagnetic (**99**) complex.

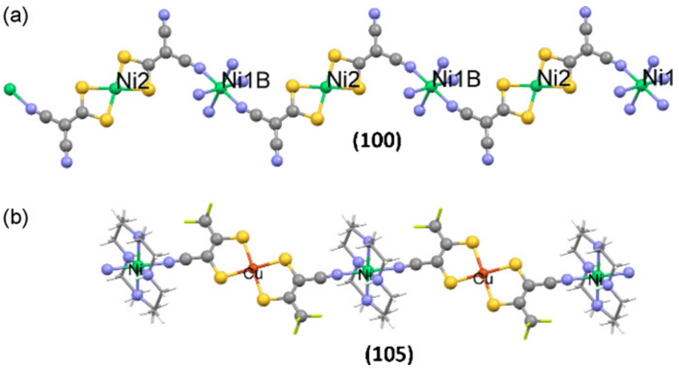


Fig. 7. Examples of 1D anion–cation chains motifs constituted by (a) a monoanionic dithiolene alternating with a monocation (**100**) and by (b) a dianionic dithiolene alternating with a dication (**105**).

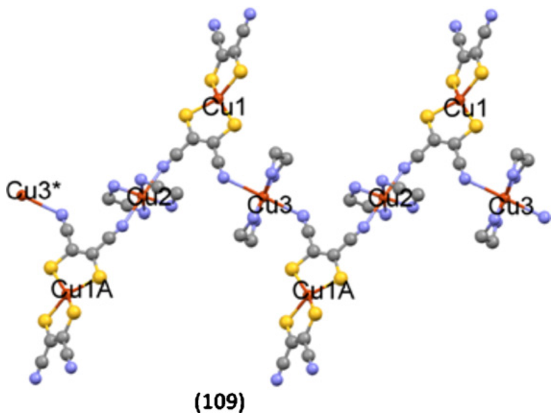


Fig. 8. 1D chain, anion–cation motif, via cis M–N intrachain interaction in (**109**).

present negligible magnetic interaction through the *mnt* bridge [71].

Trinuclear complexes—There are a few examples of trinuclear complexes in which one dianion dithiolate coordinates to two cations through the cyano groups. Among the diamagnetic trinuclear complexes already isolated and structurally characterized are the compounds [K(Me$_2$Benz$_2$18C6)]$_2$[Ni(*i*-mnt)$_2$]·2CH$_3$CN [72] (**93**) (Fig. 6, left), [K(DC18C6-B)]$_2$[Pd(*i*-mnt)$_2$] [73] (**94**), [Na(18C6)]$_2$[Ni(tfads)$_2$]·2MeOH [16] (**95**), [Na(18C6)]$_2$[Ni(mnt)$_2$][18C6]·2H$_2$O [74] (**96**) or [Na(18C6)]$_2$[Hg(mnt)$_2$] [75] (**97**). There are also similar paramagnetic complexes reported such as: [Ni(Me$_4$cyclam)]$_2$[Co(mnt)$_2$]$_2$ [76] (**98**) and [Na(18C6)]$_2$[Cu(*i*-mnt)$_2$] [77] (**99**) (Fig. 6, right), however only for the first one temperature-dependent magnetisation measurements were reported which show weak antiferromagnetic interactions.

4.1.2. Coordination polymers: 1D chains

Anion–cation chains—Some bisdithiolene complexes can act as bridging ligands through metal–N interactions in one-dimensional chain arrangements. Its possible to identify more than one type of such 1D chains. In the simplest pattern, a dithiolene anion alternates with a cation in a anion–cation chain. If the dithiolene is monoanionic, to ensure chain charge neutralization, the cation is monocationic, as in the case of [Ni(NH$_3$)$_4$][Ni(*i*-mnt)$_2$] [78] (**100**) (Fig. 7a), [Na(DC18C6-B)][Ni(mnt)$_2$] [79] (**101**), [(18C6)Na][Ni(tfadt)$_2$] [16] (**102**), [MnTPP][Ni(mnt)]$_2$ [80] (**103**), [MnTPP][Ni(adt)$_2$] [80] (**104**). In all these cases each cation unit is coordinated on both sides by the CN groups of two monoanionic dithiolene complexes, giving rise to heterobimetallic chains with alternating cation units and bisdithiolene anion units.

If the dithiolene is dianionic, to ensure a neutral 1D anion–cation chain, the cation should be dicationic. This is the case of [Ni(cyclam)][Cu(tfadt)$_2$] (**105**) (Fig. 7b) where the one-dimensional chains through CN–Ni coordination, avoid any direct (antiferromagnetic) overlap between the dithiolene complexes and a ferromagnetic intrachain interactions between the $S = 1/2$ [Cu(tfadt)$_2$]$^{2-}$ and the $S = 1$ [Ni(cyclam)]$^{2+}$ units is observed [17]. This is also the case of the rare earth compounds [{CuL^1}$_2$Gd(O$_2$NO){Ni(mnt)$_2$}]·CH$_3$OH·CH$_3$CN (**106**) and [{CuL^1}$_2$Sm(O$_2$NO){Ni(mnt)$_2$}]·2CH$_3$CN (**107**) L^1 = N,N′-propylene-di(3-methoxysalicylideneiminato). Their structure consist on almost linear trinuclear [Cu$_2$Gd] or [Cu$_2$Sm] units, which are connected through [Ni(mnt)$_2$]$^{2-}$ bridges. The [Ni(mnt)$_2$]$^{2-}$ ion coordinates through two trans cyano groups into the apical positions of two copper ions of the to two [Cu$_2$Gd]/[Cu$_2$Sm] units, making zigzag chains [69].

Most often, as in the above mentioned examples, there is charge neutralization in the chains, but there are also cases were the chains are charged, requiring the presence of additional conterions as in the case of [Na(18C6)][Na(18C6)(H$_2$O)][Cu(mnt)$_2$] [74] (**108**). In this compound [Cu(mnt)$_2$]$^{2-}$ complex dianion bridges [Na(18C6)]$^+$ cations by Na–N interactions and an extra cation [Na(18C6)(H$_2$O)]$^+$ balances the charge in crystal. On this compound the metal–N interaction in the chain involve the N atoms on the same side of the Cu bisdithiolene complex. A similar cis metal–N interaction in the chains was also observed on the [Cu(C$_2$H$_8$N$_2$)$_2$][Cu(mnt)$_2$] [81] (**109**), by Cu–N (nitrile) bonds to form a one-dimensional chain that in this case is neutral (Fig. 8).

The compound [{Mn$^{II}{}_2$Mn$^{III}{}_2$(hmp)$_6$(CH$_3$CN)$_2$}{Pt(mnt)$_2$}$_2$][Pt(mnt)$_2$]$_2$·2CH$_3$CN (**110**), comprises four [Pt(mnt)$_2$]$^{n-}$ units, in addition to a common MnII$_2$MnIII$_2$ double-cuboidal unit, [Mn$^{II}{}_2$–Mn$^{III}{}_2$(hmp)$_6$(CH$_3$CN)$_2$]$^{4+}$ = [Mn$_4$]$^{4+}$. Among the [Pt(mnt)$_2$]$^{n-}$ units, two units are coordinated with the [Mn$_4$]$^{4+}$ unit, forming a 1D chain of $\cdots$[Mn$_4$]–[Pt(mnt)$_2$]$_2\cdots$. The other two [Pt(mnt)$_2$]$^{n-}$ units form a stacking column with the coordinating [Pt(mnt)$_2$]$^{n-}$ units, constructing hybrid frames of aggregates consisting of [Mn$_4$]$^{4+}$ and [Pt(mnt)$_2$]$^{n-}$ units [70].

[Na(18C6)][Ni(*4*-pedt)$_2$]·2H$_2$O [21] (**111**) was the first reported case of a 1D anion–cation chain with a 4-pedt dithiolene complex unit. However, in this compound the N atom is not directly coordinated to the metal cation sphere coordination but instead to two water molecules coordinated to the Na cation one on each side. The chain-like anion–cation arrangement is in this case governed by a hydrogen bond N$\cdots$H–O rather than by a N–M coordination bond (Fig. 9).

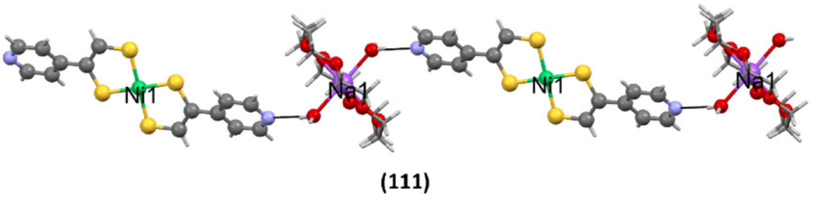
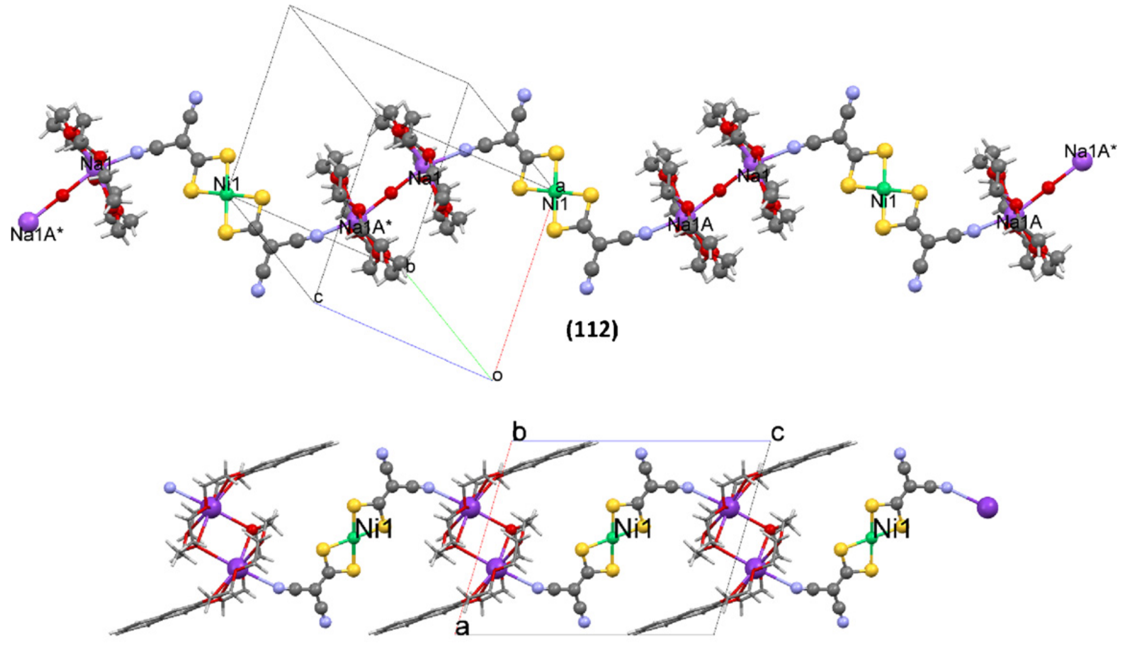


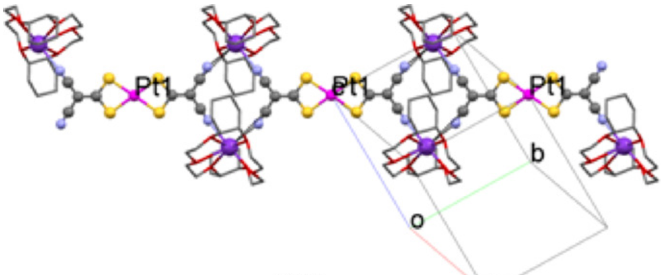
Fig. 9. 1D chain, anion–cation motif, of complex **111**.



(112)

(113)

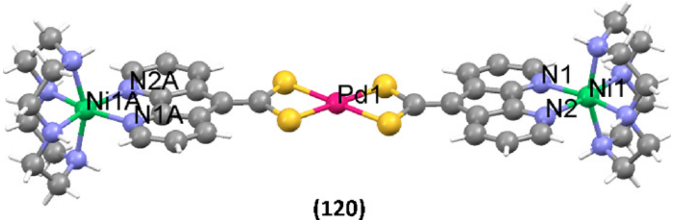
Fig. 10. 1D chain, anion–cation–cation–anion, complexes **112** and **113**.



(117)

Fig. 11. 1D chain, anion–cation–cation–anion, complex (**117**).

...Anion–cation–cation–anion... chains I—The supramolecular arrangement of complexes such as [Na(18C6)]$_2$[Ni(*i*-mnt)$_2$] [82] (**112**), [K(N18C6)]$_2$[M(*i*-mnt)$_2$] (M = Ni, Pt, Pd) [83] (**113–115**) and [K(18C6)]$_2$[Zn(mnt)$_2$] [75] (**116**) also consists in 1D chains. However, in these cases the chain charge neutralization is ensured by a anion–cation–cation–anion 1D motif. The bisdithiolene dianionic complexes are bridging pairs of cationic units connected M–O interactions. The oxygen atom can be either from a water solvent molecule (Fig. 10, **112**) or from the macrocyclic ligand (Fig. 10, **113**).

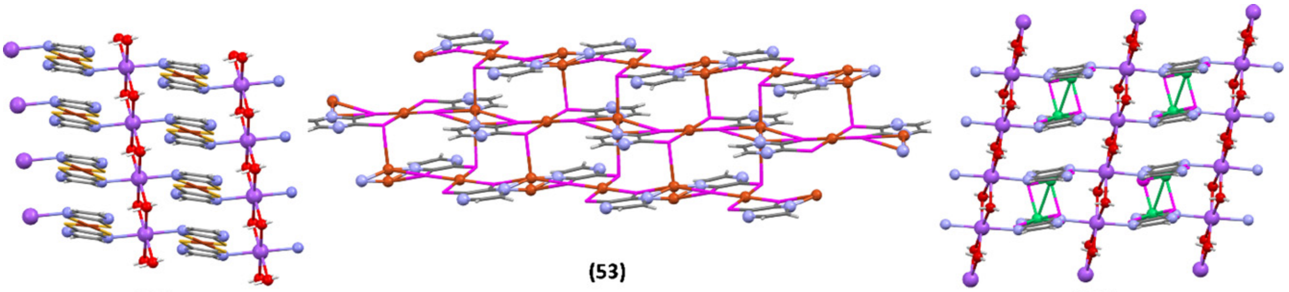


(120)

Fig. 13. Molecular scheme of [(Nicyclen)$_2$Pd(L$_2$)$_2$]$^{2+}$ in **120**.

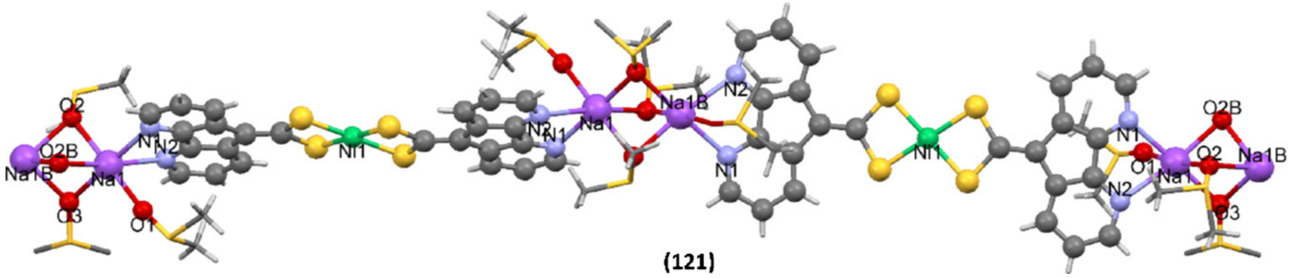
...Anion–cation–cation–anion... chains II—A second type of arrangement on this 1D anion–cation–cation–anion motif is when the two cations are not adjacent to each other. The bisdithiolate complex must necessarily have two N coordination sites on each side of the complex. In this case the dianionic bisdithiolenes bridge two monoanionic cations at each end through two N–M–N interactions in the chains (Fig. 11). Several structures with this motif have been reported [73,83–91]. An example [K(DC18C6-A)]$_2$[Pt(*i*-mnt)$_2$] [73] (**117**) is illustrated in Fig. 11.

With this same chain motif there are some cases where the chains are charged as in [Mg(15C5)]$_2$[Ni(*i*-mnt)$_2$]Cl$_2$ [87] (**118**), where two extra Cl ions per unit formula ensure charge neutrality.



(48) (53) (57)

Fig. 12. Pyrazine side coordination structures in **48**, **53** and **57**.



(121)

Fig. 14. One-dimensional chain complex [Ni(L_2)Na_2·5DMSO] (**121**).

In some cases these 1D chains are themselves assembled into 2D or even 3D networks through either interchain π–π stacking interactions, hydrogen bonds or other relevant interactions as observed in the complexes **101**, **113**–**115** and **119** ([K(18C6)]$_2$[Cu(*i*-mnt)$_2$]·CH_2Cl_2) [79,83,92].

4.2. *Pyrazine side coordinated polymers*

The complexes based on *pdt* and *pds* ligands with Ni and Cu show a remarkable capability to side coordinate alkaline metal ions such as Li^+, and Na^+ or even Cu^+ as shown in the examples of Fig. 12. These complexes were obtained directly following a standard procedure with treatment of the ligand precursors with LiOH or NaOH; Li [Cu(pds)$_2$]·3H_2O [35] (**50**), Na [Cu(pds)$_2$]·2H_2O [35,93] (**51**) Na [Cu(pdt)$_2$]·2H_2O [35] (**48**) Na_2[Ni(pds)$_2$]·2H_2O [38] (**56**) Na_2[Ni(pds)$_2$]$_2$·4H_2O [38] (**57**), and Cu^I[Cu^{III}(pds)$_2$] [37] (**53**). The last compound with side coordinated copper by a copper complex (**53**) was obtained as a minor product by an electrocrystallisation experiment. The side coordination ability of these ligands is also present in Pt complexes with larger coordination, such as the tris, penta or hepta-1,2-diselenolene complexes [94].

The side coordination in these compounds demonstrates a new degree of freedom in crystal engineering. However the interesting possibility to coordinate magnetically active metal ions in these side positions has not yet been explored.

4.3. *4,5-Diazafluorene derivative units*

With dithiolate-4,5-diazofluorene type ligands, it was possible to form discrete metal complexes both 1,1-bisdithiolates and 1,2-bisdithiolates. These discrete metal complexes were further used to generate hetero trinuclear complexes and infinite networks as described below [58,61].

4.3.1. *Hetero trinuclear complexes*

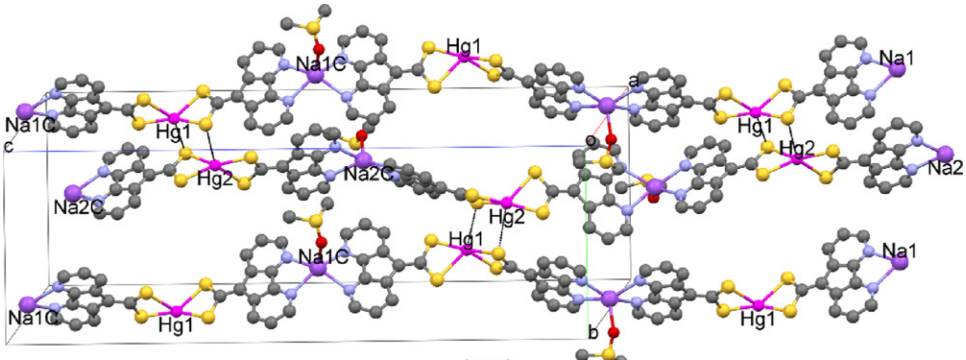
The mononuclear dianionic Pd 1,1-bisdithiolene 4,5-diazofluorene complex (**75**) was used as bridging ligand to make the trinuclear complex, [(Nicyclem)$_2$Pd(L_2)$_2$](BF_4)$_2$·6DMF (for L_2, see Table 5) (**120**) [61]. This hetero bimetallic complex contains two terminal Ni atoms and one central Pd atom. The cyclem ligand has been found effective in blocking the extra coordinating positions of the Ni^{II} atom, coordinated by the diazofluorene unit (Fig. 13).

The two Ni(II) atoms are paramagnetic with $S=1$, while the Pd atom is diamagnetic. Temperature-dependent magnetization measurements indicate a weak antiferromagnetic coupling between the Ni centers.

4.3.2. *Coordination polymers*

4.3.2.1. 1D [M$L_2$$Na_2$·5DMSO] (M = Ni, Pd). Using square-planar dianionic Ni (**73**) and Pd (**75**), 1,1-bisdithiolene complexes with the two 4,5-diazafluorene units, 1D anionic networks were obtained respectively as [Ni(L_2)Na_2·5DMSO] (**121**) (Fig. 14) and [Pd(L_2)Na_2·5DMSO] (**122**). The dianionic complexes are bridged by a sodium cation dimer bearing five DMSO molecules [61]. This same arrangement was also obtained using complex **79** (dianionic Hg 1,2-bisdithiolene complex containing two 4,5-diazafluorene units) [58]. Both coordination polymers are diamagnetic, Ni^{II} and Pd^{II}, formal oxidation state, in square-planar coordination.

*4.3.2.2. 2D networks: (Et_4N)[HgL_2NaDMSO](H_2O)$_{0.5}$ (**123**).* Following a similar procedure with **77**, a dianionic Hg 1,1-bisdithiolene complex generated in the presence of Et_4N^+ cations, only a ammonium cation was substituted by a sodium cation and it was obtained (Et_4N)[HgL_2NaDMSO]·(H_2O)$_{0.5}$ (**123**) (Fig. 15). In this case the sodium behaves as a connector between consecutive dianionic complexes giving rise to 1D anionic chains. The free spaces in the network are occupied by Et_4N^+ cations. Strong Hg-S short contacts



(123)

Fig. 15. Two-dimensional network in complex **123**. The (Et_4N) cations were omitted for clarity.

connecting adjacent chains and the overall arrangement can be described as a 2D network [61].

5. Conclusions

It becomes evident from the above described examples that during the last years a significant number of new dithiolene ligands containing N coordinating atoms and the corresponding dithiolene complexes have been developed. The capability of these bisdithiolene complexes with N coordinating atoms to bind different atoms has been already demonstrated in a few cases, where structures of increasing complexity like hetrometallic networks have been developed. However the potential to obtain novel coordination architectures based on these ligands is still far from being exhausted, especially where the coordination of different paramagnetic d-transition metal ions is concerned. The coordination of paramagnetic d-transition metal ions can be quite promising in the context of magnetic materials. In the next years significant advances both in the syntheses of ligands with more specific coordination characteristics, and in the control of their capability to selectively bind to different metals, are expected to lead to new and more complex structures including interesting magnetic materials.

Acknowledgments

The authors wish to thank their co-workers for their collaboration in this field, particularly S.I.G. Dias, I.C. Santos, R.T. Henriques, M. Formigué and J.D. Wallis. The financial support from Fundação para a Ciência e Tecnologia (contract PTDC/QUI/64967/2006), COST D35 and MAGMANet network of excellence is gratefully acknowledged.

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