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Metal bis-1,2-dithiolene complexes in conducting or magnetic crystalline assemblies

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Contents

Abbreviations: BDNT, 4,9-bis(1,3-benzodithiol-2-ylidene)-4,9-dihydronaphtho[2,3-c][1,2,5]thiadiazole; bdt, benzene-1,2-dithiolate; bds, *o*-benzenediselenolate; BEDO-TTF, bisethylenedioxytetrathiafulvalene; BEDT-TTF, bisethylenedithiolenetetrathiafulvalene; BET-TTF, bis-(ethylenethio)tetrathiafulvalene; BQ, 6,7,8,9-tetrahydrodipyrido[1,2-a:2,1-c][1,4]diazocinium; ddt, 1,4-dithiin-2,3-dithiol; dddt, 5,6-dihydro-1,4-dithiin-2,3-dithiolate; ddtdt, 6,7-dihydro-5H-1,4-dithiepine-2,3-dithiolate; dphdt, 5,6-diphenyl-1,4-dithiin-2,3-dithiolate; diotte, 1,3-dioxolane-tetrathiaethylene; edt, ethane-1,2-dithiolate; dmise, 4,5-disulfanyl-1,3-dithiole-2-selenonate; DT-TTF, dithiopheno-tetrathiafulvalene; dmid, 2-oxo-1,3-dithiole-4,5-dithiolate; dmit, 2-thioxo-1,3-dithiole-4,5-dithiol; diod, 1,2,6-oxadithiepin-4,5-dithiolato(2-)-S4,S5; EDT-TTF, ethylenedithiotetrathiafulvalene; dsit, 4,5-diselanyl-1,3-dithiole-2-thionate; F_2pdt, 2,2-difluoro-1,3-propanediyldithioethylene-1,2-dithiolate; Hpy, pyridinium; ITTF, 4-iodo-tetrathiafulvalene; MV, methylviologen (1,1′-dimethyl-4,4′bipyridinium); mnt, Maleonitriledithiolate; medt, 5,6-dihydro-6-methyl-1,4-dithiin-2,3-dithiolate; mdt, 1,3-dithiole-4,5-dithiolate; nqdt, naphthoquinonedithiolate; pdt, propane-1,2-dithiolate; phdt, 5,6-dihydro-5-phenyl-1,4-dithiin-2,3-dithiolate; per, perylene; pet, perilo[1,12-*b*,*c*,*d*]thiophene; qdt, quinoxaline-2,3-dithiolate; tcdt, tetrachlorobenzenedithiolate; TCNE, tetracyanoethylene; tdas, 1,2,5-thiadiazole-3,4-dithiol; tfd, bis(trifluoromethyl)ethylenedithiolate; tim, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; tmdt, trimethylenetetrathiafulvalenedithiolate; TMTSF, tetramethyltetraselenafulvalene; ttdt, 5,7-dihydro-1,4,6-trithiin-2,3-dithiol; TTF, Tetrathiafulvalene.

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Abstract

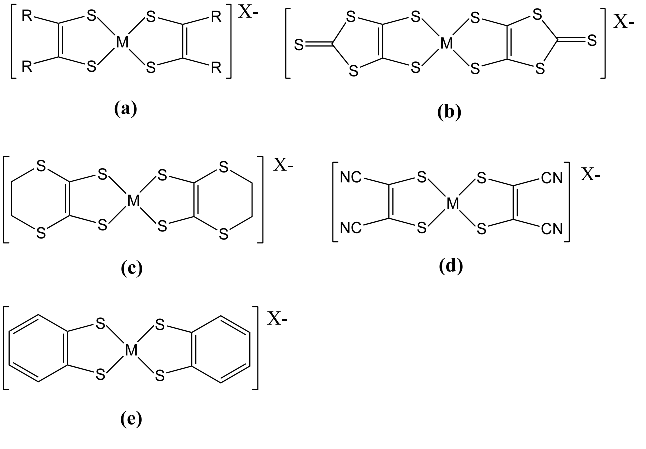
Crystalline materials studied for their conducting or magnetic properties based on metal complexes of 1,2-dithiolene ligands are discussed emphasising the wide diversity of ligands now available and the variety of materials prepared from these. Complexes have been prepared using electronically delocalised dithiolene ligands where the core complex is extended with units such as thioethers, aromatics, tetrathiafulvalene (TTF) and other heterocycles to explore the influence of these variations on the solid-state structures and properties derived from them. Although superconductivity in dithiolene complexes has so far been limited to $[M(dmit)_2]^{X-}$ salts, other ligand systems have given rise to numerous conducting and metallic salts and have proven informative in rationalising the criteria for design of the molecular units. Novel material properties have been observed in systems such as hybrid conducting | magnetic materials and mixed dithiolene-metallocene salts. In particular, highly conducting and metallic single-component materials have recently been found uniquely within materials based on metal-bis-1,2-dithiolene complexes. Magnetic materials containing dithiolene-complex building blocks have yielded systems such as ferromagnets, ferrimagnets, metamagnets and spin ladders in addition to other model systems suitable for the study of magnetic ordering. These can involve systems where the dithiolene complex is the only paramagnetic component in addition to more complex systems involving other types of building block.

Keywords: Dithiolenes; Magnetism; Conductivity; Molecular materials; Delocalisation

1. Introduction

Bis-1,2-dithiolene complexes of transition metals (Fig. 1(a)) have been widely studied due to novel properties and application in the areas of conducting and magnetic materials, dyes, non-linear optics, catalysis and others. These applications arise due to a combination of functional properties, specific geometries and intermolecular interactions. Over the last decade, a large number of new dithiolene ligands and resultant complexes have been prepared in the desire to vary and optimise the molecular properties in an effort to prepare novel and improved materials. This interest, fired by the discovery of phenomena such as superconductivity and ferromagnetism in metal dithiolene salts, has resulted in the search for new analogues with better properties. Such research has lead to a large body of recent information on both the individual dithiolene complexes and the functional materials derived from them.

This review is concerned with an overview of the range of metal dithiolene complexes now under study and a comparison of how the ligand and complex characteristics lead to new magnetic and conducting molecular materials. Related reviews have focused largely on systems known to be capable of forming superconducting solids. In particular the $[M(dmit)_2]^{X-}$ (M = Ni, Pd, Pt) (Fig. 1(b)) species have been the subject of several reviews. The preparation and conducting properties of $[M(dmit)_2]^{X-}$ salts were discussed by Cassoux et al. in 1991 [1], 1997 [2] again in 1999 [3], and aspects of the coordination chemistry of these and the Se-containing analogues were reviewed by Pullen et al. in 1999 [4]. $[Ni(dmit)_2]^{x-}$ salts with supramolecular conterions were reviewed by Nakamura et al. in 1999 [5] and aspects of the physics of $[M(dmit)_2]^{x-}$ and some $[M(dddt)_2]^{X}$ (Fig. 1(c)) salts were reviewed by Canadell et al. in 1999 [6]. In addition, $[M(mnt)_2]^{x-}$ (M = Ni, Pd, Pt) salts (Fig. 1(d)) were discussed in terms of their conducting properties by Clemenson in 1990 [7] and some of the fundamental properties of metal bis-1,2-dithiolenes appeared in earlier reviews by Burns et al. [8], McCleverty [9] and Mueller-Westerhof et al. [10].



(a) (b) (c) (d) (e)

Fig. 1. (a) $[M(dithiolene)_2]^{X-}$, (b) $[M(dmit)_2]^{X-}$,(c) $[M(dddt)_2]^{X-}$, (d) $[M(mnt)_2]^{X-}$, (e) $[M(bdt)_2]^{X-}$.

The fact that these recent reviews have focused almost entirely on $[M(dmit)_2]^{-}$ and immediate structural analogues has meant that a large number of related dithiolene species and the materials prepared from them have thus remained outwith any recent review. Such species, however, have enjoyed increasing use in the design and preparation of new conducting materials, magnetic materials and hybrid organic | inorganic or conducting | magnetic systems. Our aim is to address this body of work with an assessment of the diversity of such dithiolene complexes and how their properties give rise to cooperative electronic materials and thus to compliment the above reviews. General features of the material properties will be presented with references to more detailed physical discussion. Complexes such as $[M(dmit)_2]^{x-}$ will be dealt with here only for comparison with related complexes and for more thorough discussion, readers are referred to the above works.

Work involving dithiolene ligands spans an enormous body of research and some limits must be set in order to achieve a coherent review. The review is concerned only with species with potential as building blocks in magnetic and conducting materials and, therefore, mainly with complexes possessing unpaired electrons, except where comparison requires consideration of related diamagnetic species. Furthermore, as we are principally concerned with conducting and magnetic materials where some structure–property relationships can be understood, the focus will be mainly upon complexes that have been the subject of single crystal X-ray structure determination. The planar nature of metal-bis-1,2-dithiolenes has led these to be the most widely studied due to their capability for intermolecular interaction via π-stacking in comparison with other classes of complex containing the 1,2-dithiolene unit and discussion is, therefore, limited to these and closely related species and topics such as tris-1,2-dithiolenes [11,12] will not, in general, be included. A number of interesting complexes and materials have been prepared based on [M(dithiolene)(Cp)] type systems including such materials as a spin-ladder [13], however, these have been recently reviewed [14] and will not be further discussed here. A range of bis-1,2-dithiolene complexes have been studied in the search for specific optical properties such as third order NLO and q-switch dyes for lasers [15] and this area will not be discussed except where the compounds studied overlap with the field of conducting and magnetic materials.

Metal-bis-1,2-dithiolene complexes possess an extended electronically delocalised core comprising the central metal, four sulphurs and the C=C units. In many cases, the delocalisation can be further extended by choice of appropriate R groups (Fig. 1(a)). This delocalisation can lead to a number of important properties.

(i) Electrochemical behaviour often with one or more reversible redox processes.
(ii) Low energy absorption in the visible or NIR region.
(iii) Distribution of the frontier orbitals over much, or all, of the molecule.
(iv) In most cases, a planar arrangement of the complex with a variety of central metals. Examples include Ni, Pd, Pt, Co, Fe, Au and Cu.
(v) The large sulphur atoms compose part of the delocalised core and as such can mediate intermolecular interactions.

The combination of the above electronic and structural properties allows the design and assembly of cooperative electronic materials such as conducting and magnetic solids. The choice of central metal and ligand and associated redox properties allows the optimisation of the individual molecular characteristics and of the cooperative behaviour between these centres arising from S···S and M···S mediated intermolecular interactions facilitated by the large degree of molecular planarity. The presence of counterions in the majority of these cooperative electronic systems allows an important mechanism for variation and control of the material properties. Not only will the size and shape of the counterion control the packing and hence the intermolecular interactions, but the counterion can also be used to introduce additional functionality into the material to prepare hybrid functional systems such as molecular metals with paramagnetic counterions.

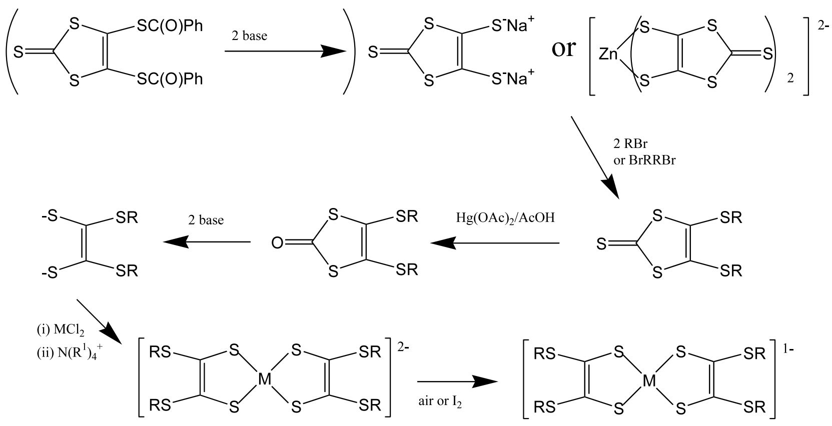
Materials where the complex possesses a formally fractional oxidation state can possess a partially-filled conduction band constructed by overlap of frontier orbitals via short intermolecular S···S and S···M contacts leading in some cases to metallic conductivity or highly conducting semiconductors. Techniques for the preparation of such non-integral oxidation state materials include electrocrystallisation and metathesis and have been described elsewhere [2]. Alternatively, in materials where the unpaired electrons remain localised, the strong intermolecular interactions can lead to cooperative magnetic phenomena and this is more likely to occur in integral oxidation-state salts.

2. $[M\{S_2C_2(SR)_2\}_2]^{X-}$

Metal-bis-1,2-dithiolene complexes with SR groups attached at the periphery generally contain a planar central core comprising eight sulphur atoms in addition to the central metal and the unsaturated carbons. Thus an extended, delocalised framework can be achieved with multiple heteroatoms to promote intermolecular interactions similar to the $[M(dmit)_2]^-$ complex family. This, along with the establishment of straightforward synthetic routes (Scheme 1 or related routes) to such species has led to the investigation of a range of complexes prepared in an attempt to mimic or better the conductivity properties of the $[M(dmit)_2]^{X-}$ salts. Ligands can be readily prepared from the Na_2dmit or the $[Zn(dmit)_2]^{2-}$ precursors with a variety of alkyl and other end functionalities according to Scheme 1. Many of the most thoroughly studied examples of ligands derived by this or related methods are shown in Fig. 2 and complexes based on these are shown in Tables 1 and 2.

2.1. *$[M(dddt)_2]^X$*

The first $(dddt)_2$-based complex was reported by Vance et al. in 1985 [16] with the formula $[NEt_4][Ni(dddt)_2]$ (**1**) derived from the precursor $C_5H_4S_5$ thione (5,6-dihyrdo-1,3-dithiolo[4,5,6][1,3]-dithiin-2-thione by hydrolysis with KOH affording the salt K_2dddt [16]. Other 1:1 salts **2** and **3** were later prepared



Scheme 1. Preparation of $[M\{S_2C_2(SR)_2\}_2]^{2-/1-}$.

with **1** and **2** showing enhanced magnetic interactions over **3** due to inclusion of the smaller counterions. A principal motivation for exploring $[M(dddt)_2]^X$ complexes lies in the similarity to bisethylenedithiolenetetrathiafulvalene (BEDT-TTF), the organic electron donor known to have led to the largest number of superconducting organic salts and those with the highest T_c (Fig. 3(b)). It has long been recognised that metal-bis-1,2-dithiolenes have in general, a similarity to organic electron donors of the tetrathiafulvalene (TTF) family (Fig. 3) with the central metal in place of the C=C bond, however, the particular similarity of $[M(dddt)_2]$ to BEDT-TTF has made it especially attractive for study.

$[Ni(dddt)_2]^X$ complexes have been synthesised with a range of counterions with the charge on the complex ranging between diaanionic, monoanionic, neutral and fractional-oxidation-state cationic species [21]. Salts that have been structurally characterised and where the stoichiometry was given with confidence are listed in Table 1. The references given also include examples of salts with other counterions where some doubt about the stoichiometry of the salt was expressed and these are not listed in Table 1. $[Ni(dddt)_2]^-$ shows two reversible redox processes between dianionic and neutral complexes at ca. -0.7 and 0.0 V (vs. Ag/AgCl). A further oxidation is associated with the formation of partially oxidised, conductive compounds containing positively charged $[Ni(dddt)_2]^{X+}$. This contrasts with other fractional oxidation state metal-bis-1,2-dithiolene complexes, in particular those of $[M(dmit)_2]^{X-}$, which generally have a charge between 0 and $1-$ and provides another similarity with the BEDT-TTF series of salts where the organic species bears a fractional positive charge. Thus uniquely among metal-bis-1,2-dithiolene complexes, salts isostructural to the organic analogue have been prepared with the same counterion.

In this context, salt **4** and its isostructural analog, $[BEDT\text{-}TTF]_3[HSO_4]_2$, are both metallic at room temperature (r.t.) and exhibit metal to insulator transitions at 25 and 130 K, respectively. The salt **5** also shows metallic behaviour down to at least 1.3 K. This similarity with organic analogues has allowed study of structurally related salts that have a marked difference in the electronic nature of the component molecules. This leads to differences in material properties that have their origin in the differences in the frontier orbitals of the molecules. Thus, the influence of a much smaller HOMO/LUMO separation in $[Ni(dddt)_2]^{X-}$ (and in Ni-bis-1,2-dithiolenes in general) than the organic analogues and the influence of these orbitals on the dimensionality of the salt play a key role in determining the conductivity properties. The salts **6** and **7** both show triads of the metal complexes with the intratriad interaction for **6** much stronger than that of **7** leading to much lower conductivity for **6**.

In comparison, more salts of $[Pd(dddt)_2]^X$ show metallic or semi-metallic behaviour and this has been examined by Canadell et al. [6] who have deduced that partially filled bands of these salts depend upon the

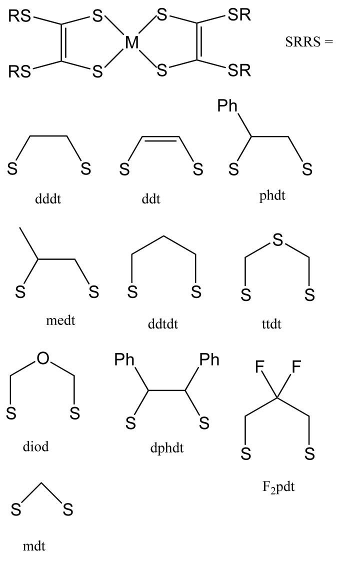


Fig. 2. Derivitisations of $[M(S_2C_2(SR)_2)_2]^{X-}$.

Table 1
Salts containing $[M(dddt)_2]^X$ complexes

	Complex	References
1	$[NEt_4][Ni(dddt)_2]$	[16–19,30,49]
2	$[NMe_4][Ni(dddt)_2]$	[20]
3	$[NBu_4][Ni(dddt)_2]$	[17]
4	$[Ni(dddt)_2]_3[HSO_4]_2$	[22–24]
5	$[Ni(dddt)_2]_3[AuBr_2]_2$	[25,26]
6	$[Ni(dddt)_2]_3[ClO_4]_2$	[27]
7	$[Ni(dddt)_2]_3[BF_4]_2$	[28,27,29]
8	$[TTF][Ni(dddt)_2]$	[21]
9	$[Pd(dddt)_2][Ag_{1.54}Br_{3.50}]$	[31,32]
10	$[Pd(dddt)_2]_2[AuBr_2]$	[33,26,35]
11	$[Pd(dddt)_2]_2[SbF_6]$	[26]
12	$[Pd(dddt)_2]_2[PF_6]$	[26]
13	$[Pd(dddt)_2]_2[TeCl_6]$	[33]
14	$[Pd(dddt)_2]_2[GaBr_4]$	[34]
15	$[Pd(dddt)_2]_2[IBr_2]$	[26]
16	$[Pd(dddt)_2]_2[CF_3SO_3]$	[36]
17	$[Et_4N][Pt(dddt)_2]$	[37]
18	$[Pt(dddt)_2]_3[BF_4]_2$	[27]
19	$[Pt(dddt)_2]_2[IBr_2]$	[27,26]
20	$[Pt(dddt)_2]_2[ICl_2]$	[27]
21	$[Pt(dddt)_2]_2[AuBr_2]$	[27]
22	$[Au(dddt)_2]$	[17]
23	[TTF][Au(dddt)2]	[38]
24	$[NBu_4]_2[Co(dddt)_2]_2$	[39]
25	$[Ni(dddt)_2][FeCl_4]$	[32]
26	$[Ni(dddt)_2][FeBr_4]$	[32]
27	$[Au(dddt)_2][FeCl_4]$	[32]
28	$[Au(dddt)_2][FeBr_4]$	[32]
29	$[Pt(dddt)_2][FeCl_4]$	[32,40]
30	$[Pt(dddt)_2][FeBr_4]$	[32]
31	$[Ni(dddt)_2]_x[Ni(dmit)_2]_y$	[19]
32	$[Pt(dddt)_2][Ni(dmit)_2]_2$	
33	$[Ni(dddt)_2]_x[Pd(dmit)_2]_y$	
34	$[Pt(dddt)_2]_x[Pd(dmit)_2]_y$	

extent of dimerisation in the solid state such that better electrical conductivity is expected for weakly dimerised systems. Synthesis of **9** yields a stable molecular metal at r.t., remaining metallic down to 4.2 K. The structure of the salt contains layers of donor cations alternating with layers of silver bromide complex anions along the crystallographic *a*-axis of the unit cell. The Ag and Br atoms are disordered in the anion layer. The conducting layers contain uniform stacks of the translationally equivalent $[Pd(dddt)_2]^{x+}$ cations along the *c*-axis. Within the cation layers there are short interstack S···S contacts. Other salts containing $Pd(dddt)_2$ units that show metallic or semi-metallic properties include **10**, **11**, **12**, **15** and several salts with a composition not completely determined [26].

In contrast, the radical cation salt **14** shows conductivity that decreases as temperature decreases from a r.t. value of 0.25 S cm^{-1}. The crystal structure of the salt contains stacks of $[Pd(dddt)_2]$, with a Pd···Pd distance of 3.011 Å. The cation layers alternate with layers of $[GaBr_4]^-$ along the *c*-axis of the unit cell. Other $[Pd(dddt)_2]^X$ complexes displaying semi-conducting behaviour including **16**, which consists of layers of dimerised $Pd(dddt)_2$ radical cations [Pd···Pd = 3.031(2) Å] with disordered $[CF_3SO_3]^-$ anions located between the layers (Fig. 4).

In solution, $[Pt(dddt)_2]^X$ complexes behave in a very similar manner to the Ni analogs with the same type of reversible electrochemistry and, therefore, access to the same range of oxidation states. This also allows the formation of salts with the metal complex in a fractional positive oxidation state and the salts **18**, **19**, **20** and **21** have been structurally characterised. Salt **18** is isostructural with $[BEDT\text{-}TTF]_3[BF_4]_2$ and **19**, **20** and

Table 2
Salts containing $[M\{S_2C_2(SR)_2\}_2]^{X-}$ complexes other than $[M(dddt)_2]^X$

	Complex	References
35	$[Ni(medt)_2]$	[41]
36	$[Ni(phdt)_2]$	[41]
37	$[NBu_4][Ni(dphdt)_2]$	[42]
38	$[PPh_4][Ni(dphdt)_2]$	[43]
39	$[NBu_4][Ni(ddt)_2]$	[44]
40	$[NBu_4][Pd(ddt)_2]$	[45]
41	$[NBu_4][Ni(mdt)_2]$	[46]
42	$[N^tBu_4][Cu(ddtdt)_2]$	[47,48]
43	$[NEt_4][Cu(ddtdt)_2]$	[49]
44	$[NEt_4][Ni(ddtdt)_2]$	[48]
45	$[NBu_4][Ni(F_2pdt)_2]$	[50]
46	$[NEt_4][Cu(ttdt)_2]$	[53]
47	$[N^tBu_4][Ni(ttdt)_2]$	[53]
48	$[NEt_4][Au(ttdt)_2]$	[53]
49	$[NBu_4][Pt(ttdt)_2]$	[19]
50	$[NBu_4][Pd(ttdt)_2]$	[19]
51	$[TTF][Au(ttdt)_2]$	[53]
52	$[PPh_4][Ni(diod)_2]$	[54]
53	$[PPh_4][Pd(diod)_2]$	[54]
54	$[PPh_4][Cu(diod)_2]$	[54]
55	$[PPh_4][Au(diod)_2]$	[54]
56	$[NBu_4][Ni(diotte)_2]$	[55]

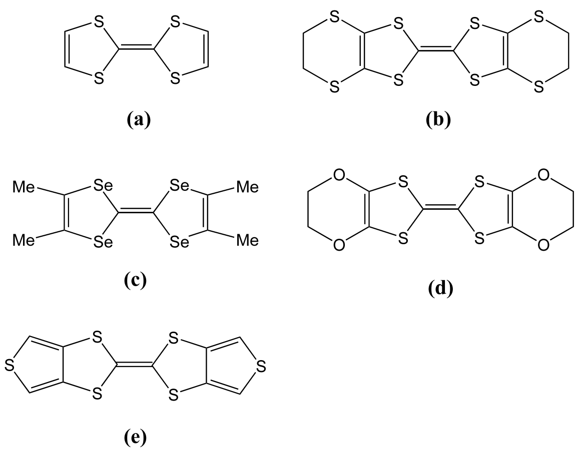


Fig. 3. Organic electron donors (a) TTF, (b) BEDT-TTF, (c) TMTSF, (d) BEDO-TTF, (e) DT-TTF.

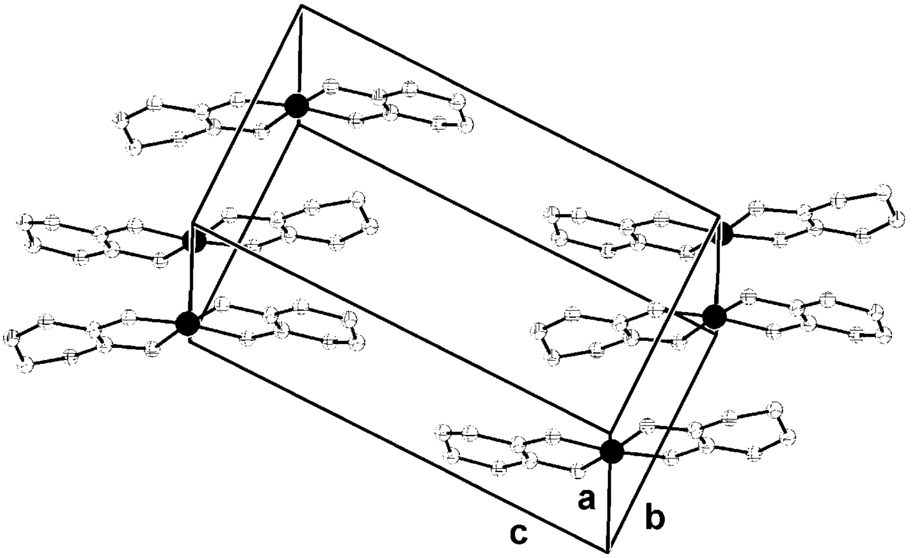


Fig. 4. A representation of X-ray crystal structure of the unit cell of, $[Pd(dddt)_2]_2[CF_3SO_3]$ **16**. The central Pd atoms are depicted as the filled black spheres, the coordinating sulphur atoms as cross-hatched spheres and the carbon atoms as octants. The disordered $[CF_3SO_4]$ anions, which are located in the void in the centre of the unit cell, are omitted for clarity.

21 are isostructural with β-BEDT-TTF salts with linear counterions, however, the internal stack structure in all cases differs from the BEDT-TTF salts with increased dimerisation of the Pt complexes. This leads to semiconductor-type behaviour.

The analogous materials containing Au, **22** and **23** have also been prepared. The former has been prepared by both chemical and electrochemical oxidation of the diamagnetic $[Au(dddt)_2]^-$ precursor and the X-ray structure indicates dimerisation leading to a diamagnetic ground state. Salt **23** contains dimerised TTF units in an arrangement inappropriate for high conductivity. The Co complex **24** was isolated as an air-sensitive solid and no structural information was obtained due to the sensitivity.

Interestingly, when $[M(dddt)_2]^+$ ($M = Pt$, Ni, Au) is crystallised with $[FeX_4]^-$ ($X = Cl$, Br) (**25**, **26**, **27**, **28**, **29**, **30**) the magnetic susceptibility shows three-dimensional (3-D) behaviour for all of these salts despite the isolated chain or sheet arrangement of the magnetic anions. This is regarded as a consequence of the coexistence of exchange paths involving the halides on the Fe and the π-electrons on the donor molecules. These salts show an antiferromagnetic transition around liquid helium temperature if $[FeBr_4]^-$ is adopted as a counter anion, and their transition temperature is also affected by substitution of the central metal atom.

The ability to isolate $[M(dddt)_2]^{X+}$ cationic species allows the formation of salts where both cationic and anionic components are composed of different metal-bis-1,2-dithiolene complexes and a range of salts of general formula $[M(dddt)_2][M'(dmit)_2]_x$ (**31**–**34**) has been prepared [19]. An X-ray structure of **32** revealed a 1:2 ratio salt containing stacks of $[Ni(dmit)_2]$ units with no short contacts between adjacent molecules. The only short intermolecular contacts were with layers of side-by-side $[Pt(dddt)_2]$ species which separated these stacks. The conductivity of all these salts was rather low at around 10^{-5}–10^{-3} S cm^{-1} and this is consistent with the lack of intermolecular contacts displayed in the structure obtained.

2.2. Other $[M\{S_2C_2(SR)_2\}_2]^{X-}$ complexes

The work on the 5,6-dihydro-1,4-dithiin-2,3-dithiolate (dddt) ligand represents the most thoroughly studied example among dithiolene ligands extended with sulphur-containing groups, excluding dmit. However, there are numerous other ligands containing the dithiolene unit extended with SR groups reported in the literature. Often, these have been prepared towards other applications such as optical materials and it would be misleading to exhaustively quote every complexes prepared. Thus, Fig. 2 and Table 2 show the principle complex families explored in recent years either involving study of materials properties or with the intention of designing new ligands for materials study. Inspection of this body of work allows some generalisations concerning this type of complex in conducting or magnetic materials.

The Ni complexes and some Pd complexes of a number of ligands have been prepared in an attempt to obtain analogous properties to those found within the dddt family and much work has focused on electrochemical and structural details. These complexes include the substituted analogues of the dddt ligand, 5,6-dihydro-6-methyl-1,4-dithiin-2,3-dithiolate (medt) (**35**), 5,6-dihydro-5-phenyl-1,4-dithiin-2,3-dithiolate

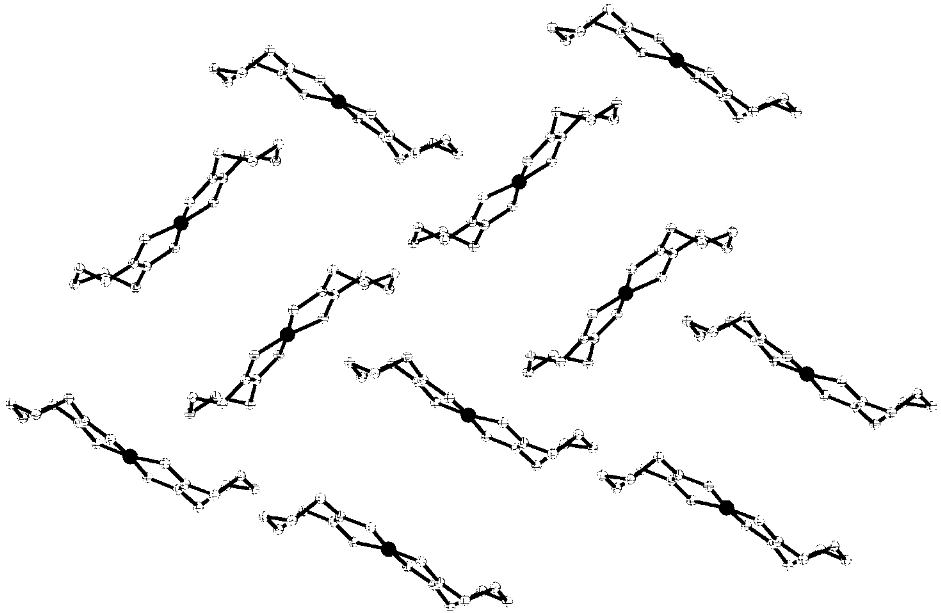


Fig. 5. A representation of a section of the crystal structure of $[NEt_4][Cu(ttdt)_2]$ **46** illustrating the chair conformation of the anions. The NEt_4 cations are omitted for clarity and the central Cu atoms are shown as black spheres, the sulphur atoms as cross-hatched spheres and the carbon atoms as octants.

(phdt) (**36**) and 5,6-diphenyl-1,4-dithiin-2,3-dithiolate (dphdt) (**37**, **38**); 1,4-dithiin-2,3-dithiol (ddt) (**39**, **40**), the unsaturated analogue of dddt; 1,3-dithiole-4,5-dithiolate (mdt) (**41**) and 6,7-dihydro-5*H*-1,4-dithiepine-2,3-dithiolate (ddtdt) (**42**, **43**, **44**), the analogues with one CH_2 unit less or more, respectively. A fluorinated analogue of ddtdt has been prepared (**45**) and used to prepare a salt with TTF that consists of alternating trimers of TTF units and trimers of dithiolene complexes. Other alkyl-substituted complexes with no linking across the S–RR–S moiety have also been prepared but these have typically been aimed towards optical and non-linear optical applications (see for example references [51,52]). In general, all these form complexes with Ni that show the expected reversible electrochemistry between the neutral, monoanionic and dianionic species. Attempts to prepare partially oxidised salts from these precursors are reported in some cases, but in general new single crystal metallic or semiconducting salts have not been obtained.

Complexes of the ligand 5,7-dihydro-1,4,6-trithiin-2,3-dithiol (ttdt) have been reported, of which the **46**, **47**, **48**, **49** and **50** have been well characterised including X-ray structures for the first four of these. These complexes show two electrochemical waves (1 – /0, 2 – / 1 –) and the conductivities of the partially oxidised species have been measured and found to be variable for the Ni complexes (between 10^{-1} and 10^{-5} S cm^{-1}, depending on counter ion and 10^{-3} S cm^{-1} for the Au complexes). The structures of these complexes show the distance between the central metal ions in the packing of the complexes is limited by the chair configuration of the end (–C–S–C–) moiety of the complexes (Fig. 5). The X-ray structure of **51** was reported, however, the molecular arrangement, which comprises two TTF units surrounded by Au complexes is not well organised for high conductivity and this along with the lack of charge transfer is reflected in the r.t. conductivity of 4.7×10^{-4} S cm^{-1}. Other attempts to prepare charge-transfer salts by metathesis or electrocrystallisation have indicated that these appear not suitable for the formation of [cation]$[Ni(ttdt)_2]$ non-integral oxidation state salts.

Anionic bis-complexes of the related ligand 1,2,6-oxadithiepin-4,5-dithiolato(2-)-S4,S5 (diod) have been synthesised with Ni, Cu, Pd and Au (**52**–**55**). The electrochemistry of these complexes was also investigated with only the Ni complex **52** having access to both reversible (1 – /0 and 2 – /1 –) waves.

In order to introduce chirality into conducting salts, complexes were prepared with the ligand 1,3-dioxolane-tetrathiaethylene (diotte) (Fig. 6). In addition to the monoanionic Ni complex **56**, the neutral Ni complex was prepared by I_2 oxidation and this was used to prepare mixed-ligand complexes $[NBu_4][[Ni(diotte)L]$, L = mnt, dmit by exchange with $[NiL_2]^{2-}$. Conductivities of these materials containing the diotte ligand and also salts prepared with dipyridinium cations were gen-

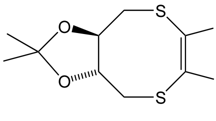


Fig. 6. Molecular structure of the ligand diotte (see compound **56**).

erally low, attributed to the steric demands of the ligand impeding close intermolecular contacts.

The aim of work in this area has generally been to modify the $[M(dmit)_2]^{X-}$ structural type to seek analogous conducting salts with the hope of observing improved superconducting properties. Although this original motivation has not been realised, a number of related aspects concerning structural and electronic features have been established and clarified. The wide range of complexes prepared in the last decade, which differ only in the alkyl or other functionality attached to the MC_4S_8 central core, indicate that even minor modifications can have a profound influence on the electronic properties of the complex, and more particularly on the solid-state packing. This in turn, leads to variation in solid-state properties from metallic conductivity to isolated non-interacting complexes.

Molecular species capable of forming superconducting crystals are composed of planar (e.g. Tetramethyltetraselenafulvalene (TMTSF), $[M(dmit)_2]$) or nearly planar (e.g. BEDT-TTF, bisethylenedioxytetrathiafulvalene (BEDO-TTF)) components. The use of bulkier or non-planar end substituents in this section has illustrated the difficulties which can ensue in the achievement of close intermolecular interactions and uniform stacking which is often required for the formation of superconducting salts. Empirically, it appears that if a ligand is to be is targeted at this property, too large a deviation from planarity is undesirable in further ligand design.

The metal-bis-1,2-dithiolenes are typically believed to possess a poorer ability to delocalise charge than the TTF-based organic electron donors based on a consideration of the electrochemical parameters, and this is an important prerequisite for the formation of metallic and superconducting salts. The most notable exceptions to this are the $[M(dmit)_2]^{X-}$ complexes, the only bis-1,2-dithiolene complexes to form superconducting salts. If superconductivity is to be achieved in another family, it appears that this consideration must be addressed and complexes with two closely-spaced, reversible electrochemical oxidations must be prepared.

The preparation of the dddt series of complexes, in addition to providing a series of metallic molecular salts for study, has offered a unique opportunity through its structural similarity with BEDT-TTF, to compare isostructural salts containing organic or inorganic molecular components. This has allowed some insight into the influence of the electronic nature of the building block on material properties. Lengthening or modifying the alkyl chain to give ddtdt, ttdt or diod has proven attractive in the search for structurally related analogues but has led to large deviations from planarity that appears to impede the formation of closely stacked complexes. Metallic conductivity may perhaps be most successfully sought in systems which retain the structural pattern of dddt complexes with CH_2 groups substituted by other groups such as S or NH or it may be that even longer alkyl substituents can allow enough flexibility to achieve the appropriate packing of complexes.

As the electrochemical and structural properties of many complexes in this section appear unsuited to the formation of superconducting or metallic salts, the study of these as components of magnetic salts or hybrid magnetic | conducting salts may prove appropriate. This would take advantage of the capability of these species to form strong intermolecular interactions along with the tendency to result in salts with localisation of the unpaired electrons.

3. $[M(mnt)_2]^{X-}$

Complexes of the maleonitriledithiolate (mnt) ligand have been one of the most widely studied families of dithiolene complexes during the past 25 years. The planar structure, typical of many related bis-1,2-dithiolene complexes, forms a highly delocalised system extending out to the CN groups at the periphery (Fig. 1(d)) and as such, complexes of the mnt ligand display an extremely versatile set of structural, chemical and physical properties [7]. The $Na_2(mnt)$ ligand was first synthesised in 1957 [56] and subsequently optimised [57] from the reation of CS_2 with NaCN in DMF, producing a stable $Na[S_2CCN]$ intermediate which was recrystallised in 2-methyl-1-propanol. The intermediate then dimerised with loss of sulphur on addition to water and the mnt product was recrystallised from ethanol. The conformation of the new mnt ligand was proven via the formation of metal complexes and then in later studies of the first complexes with divalent transition metal ions as tetraalkylammonium salts [57]. Preparation of the monoanionic radical Ni, Pd and Pt complexes, although achievable by oxidation of the dianions with I_2, can be carried out with much greater product purity through electrochemical oxidation of the dianions to form insoluble monoanionic crystalline material in the electrochemical cell. The straightforward synthesis, extended delocalisation and early establishment of mnt as a novel ligand have all contributed to its widespread and continued use in conducting and magnetic materials.

The electronic properties intrinsic to this structure have been extensively studied with various computational methods [56,58–62] including the Hückel and extended Hückel approaches to identify the nature of the orbitals involved in intramolecular and intermolecular interactions. These structural properties allow the complexes to interact in the solid state via short stacking S···S and short interstack S···S contacts. The high charge density associated with the delocalised planar π-system enables compounds based on these materials to have access to a diverse number of stacking modes in the solid state and, is, therefore, one of the most dominant factors in the determination of molecular interactions and resultant physical properties. In this section, mnt complexes with interesting structural, magnetic and conducting properties are discussed, focussing on systems studied since the publication of a review on mnt complexes in 1990 by Clemenson [7].

Early studies of paramagnetic $[M(mnt)_2]^-$ complexes mainly involved salts (Table 3) with large counterions such as tetraalkylammonium and these largely led to dimerisation of the metal complex components resulting in a non-magnetic ground state and low conductivity. Later work explored smaller alkali–metal counterions which forced the metal complexes closer together leading to equidistant stacks in some cases with greater potential for magnetically interesting or highly conducting salts [7]. A more recent study has continued work with small counterions and also planar counterions to promote close metal-complex···metal-complex interactions but has also focused on more complex systems with open-shell or structurally varied counterions. Other recent work with larger counterions **57**–**59** has shown general features in keeping with earlier studies. The particular case of metallocene salts containing $[M(mnt)_2]^{X-}$ anions is discussed in Section 9.1.

3.1. Ferromagnetic coupling

Salts involving $[Ni(mnt)_2]^-$ are extremely unusual in providing several recent examples where some ferromagnetic or weak ferromagnetic ordering appears to be apparent including one salt, **60**, where ferromagnetic ordering was confirmed below 4.5 K. This material consists of side-by-side stacks of planar $[Ni(mnt)_2]^-$ complexes forming two-dimension (2-D) sheets with these separated by a network of ammonium cations and H_2O (Fig. 7) [67]. The stack shows an equidistant arrangement of the anions, which prevents the dimerisation to a singlet ground state observed in other salts. Clearly the small counterion plays an important role in constraining the stacking into this motif. The Curie temperature, increases markedly with pressure until ferromagnetic order abruptly disappears at 6.8 kbar, indicating that the magnetic coupling is very sensitive to intermolecular separation. This was suggested, on the basis of quantum-chemical calculations, to arise from a competition between ferromagnetic coupling (resulting from nickel–sulphur intermolecular spin interactions), and antiferromagnetic coupling (from nickel–nickel interactions).

Table 3
Salts containing$[M(mnt)_2]^{X-}$ complexes

	Complex	References
57	$[PPh_4]_2[Cu(mnt)_2]$	[63]
58	$[PPh_4][Ni(mnt)_2]$	[63]
59	$[PPh_4][Fe(mnt)_2]$	[63]
60	$[NH_4][Ni(mnt)_2]\cdot H_2O$	[64–66]
61	$[BDNT]_2[Ni(mnt)_2]$	[68]
62	$[BDNT][Pd(mnt)_2]$	[68]
63	$[BDNT][Pt(mnt)_2]$	[68]
64	$[BDNT][Au(mnt)_2]$	[68]
65	$[BDNT][Au(mnt)_2]_2$	[68]
66	[Ethyl-pyridinium]$[Ni(mnt)_2]$	[69]
67	$[Hpy]_2[Fe(mnt)_2]_2$	[70]
68	$[Hpy]_2[Co(mnt)_2]_2$	[70]
69	[Na.15-crown-5]$[Ni(mnt)_2]\cdot H_2O$	[72]
70	$[Na_2$(benzo-15-crown-5)$_3(H_2O)_2]$ $\cdot[\{Ni(mnt)_2\}_2]$	[73]
71	[{Na(benzo-15-crown-5)}$_2]_n\cdot Ni(mnt)_2]$	[74]
72	$[M(tim)][Co(mnt)_2]$ (M = Ni, Cu)	[75]
73	$[PhCNSSN]_2[Pt(mnt)_2]$	[76]
74	$[(p\text{-}ClC_6H_4\text{-}CNSSN)_2Cl][Pt(mnt)_2]$	[76]
75	$[BQ][Co(mnt)_2]$	[77]
76	$[A][Ni(mnt)_2]$	[78]
77	$[NBu_4]_2[Ni(mnt)_2Cu_4I_4]$	[79]
78	$[NBu_4]_2[Pd(mnt)_2Cu_4I_4]$	[79]
79	$[NBu_4]_2[Pt(mnt)_2Cu_4I_4]$	[79]
80	[DT-TTF]$_2[Ni(mnt)_2]$	[80,81]
81	[DT-TTF]$_2[Pt(mnt)_2]$	[82]
82	[DT-TTF]$_2[Au(mnt)_2]$	[82]
83	[BET-TTF]$[Au(mnt)_2]$	[84]
84	[BET-TTF]$_2[Pt(mnt)_2]$	[84]
85	[ITTF]$_2[Pd(mnt)_2]$	[85]
86	[BEDT-TTF]$[Ni(mnt)_2]$	[88]
87α,β	$[per]_2[Ni(mnt)_2]$	[89,92]
88α,β	$[per]_2[Cu(mnt)_2]$	[89,92]
89α	$[per]_2[Pt(mnt)_2]$	[90]
90α	$[per]_2[Pd(mnt)_2]$	[91]
91α	$[per]_2[Au(mnt)_2]$	[90]
92	$[per]_2[Fe(mnt)_2]$	[94]
93	$[per]_2[Co(mnt)_2]$	[94]
94	$[per][Co(mnt)_2]\cdot 1/2(CH_2Cl_2)$	[97]
95	$[per]_4[Co(mnt)_2]_3$	[93]
96	$[pet]_3[Ni(mnt)_2]_2$	[99,100]

The preparation of charge-transfer salts between 4,9-bis(1,3-benzodithiol-2-ylidene)-4,9-dihydronaphtho[2,3-c]1,2,5thiadiazole (BDNT) and $[M(mnt)_2]^{X-}$ (**61**–**65**) was achieved both by the electrochemical oxidation of BDNT in $[NBu_4]_2[M(mnt)_2]$ solution and by slow mixing of solutions of $[BDNT][SbCl_6]_2$ with $[NBu_4]_2$-$[M(mnt)_2]$. This led to salts of varying stoichiometry with **61**–**64** showing high conductivity. In all the salts, the $[M(mnt)_2]^-$ component was shown to be monoanionic (CN stretch 2207–2220 cm^{-1}) hence the valence of BDNT is $+0.5$ (**61**); $+1$ (**62**–**64**); or $+2$ (**65**). Unfortunately, the crystal structure could be determined for only **65**, which displays criss-cross stacks of dimerised dithiolene complexes and BDNT units with a twisted central ring consistent with the low conductivity. Interestingly, **61** shows a ferromagnetic interaction with $J = 3.4$ K [68], which was concluded on the basis

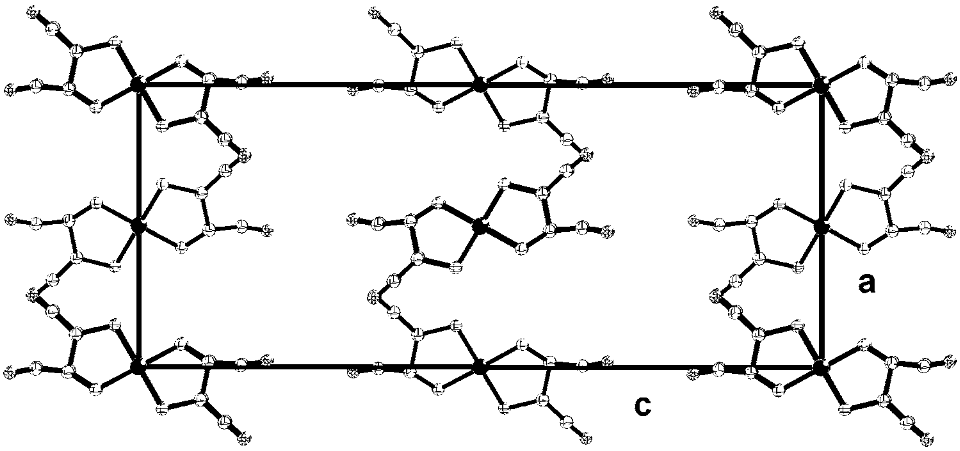


Fig. 7. A representation of the crystal structure of $[NH_4][Ni(mnt)_2] \cdot H_2O$ **60** showing side-by-side interactions between stacks. The nickel atom is represented as a black sphere, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres. The cation and the solvent water molecule were omitted for clarity.

of EPR evidence to arise from the $[Ni(mnt)_2]^-$ component. In the absence of structural data, however, further understanding of this behaviour could not be obtained.

Magnetic susceptibility measurements on the compound [Ethyl-pyridinium]$[Ni(mnt)_2]$ (**66**) show Curie–Weiss behaviour with a change in parameters at around 50 K. Above this temperature a Curie constant of 0.3 emu K mol^{-1} and a Weiss constant of -150 K were observed and below 50 K these values were 0.08 emu K mol^{-1} and $+2$ K, respectively. A maximum in the susceptibility was observed at 285 mK which, taken alongside the low value of the Curie constant suggests low temperature ordering to a phase with a non-cancelled alignment of the spins. The structure of **66** comprises three different environments for the paramagnetic anions with two in a stacking mode and one ca. orthogonal to the stack (Fig. 8). The stacking showed an ACA-type repeat unit with an inversion centre on complex C.

3.2. Antiferromagnetic coupling with closed shell counterions

A series of salts has been prepared using the related pyridinium counterion. The compounds $[Hpy]_2[M(mnt)_2]_2$ **67**, **68** were prepared by electrocrystallisation and the resulting salts are isostructural, consisting of alternately packed $[M(mnt)_2]_2$ units, with the metal in a square–pyramidal environment co-ordinated by sulphur atoms alongside pyridinium cations bridged by three-centred hydrogen bonds to the mnt ligands. Magnetic susceptibility measurements with **68** showed a small (ca. 1.5×10^{-4} emu mol^{-1} at r.t.) paramagnetism, temperature independent below 150 K (ca. 0.7×10^{-4} emu mol^{-1}), while **67** had a strong paramagnetic contribution of antiferromagnetically coupled pairs of $S = 3/2$ in the $[\{Fe(mnt)_2\}_2]^{2-}$ units, with $-2J/k_B = 515$ K [70].

Crown-ether-complexed alkali metals are promising counter ions for use in the formation of novel materi-

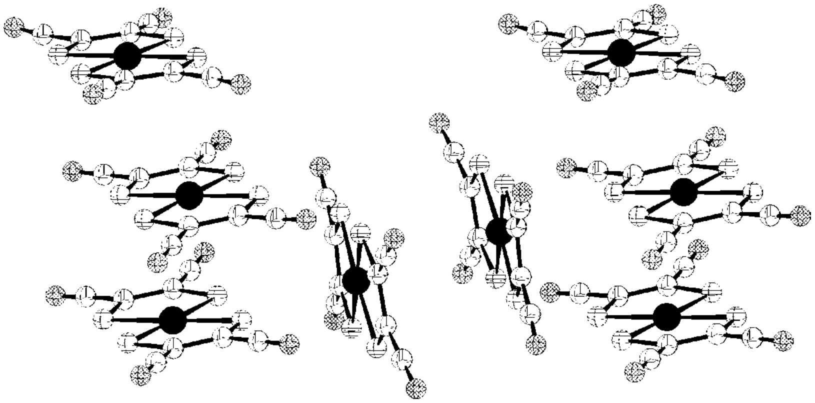


Fig. 8. A representation of the crystal structure of [Ethyl-pyridinium]$[Ni(mnt)_2]$ **66** showing stacking and non-stacking anions. The nickel atom is represented as a black sphere, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres. The cations were omitted for clarity.

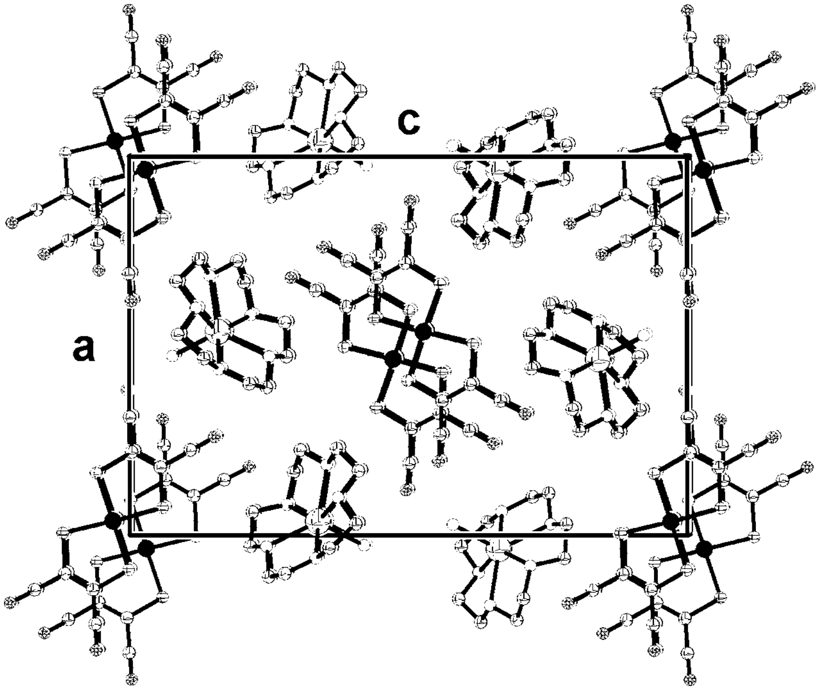


Fig. 9. A representation of the crystal structure of [Na.15-crown-5][Ni(mnt)$_2$]·H$_2$O **69**. The nickel atom is represented as a black sphere, the sodium atoms by large octant spheres, the oxygen atoms by the open spheres, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres.

als, for example the salt [Li$_{0.6}$(15-crown-5)][Ni(dmit)$_2$]$_2$·H$_2$O displays both electronic and ionic conductivity [71]. It is, therefore, possible that the use of mnt-based complexes with crown ethers may also provide an interesting route to new materials. In this context, **69** has been prepared by electrocrystallisation and characterised by X-ray crystallography showing a stacking arrangement of [Ni(mnt)$_2$]$^-$ with slight dimerisation between the anions, as indicated by magnetic susceptibility measurements, and a slipped stack arrangement of the crown ethers (Fig. 9) [72].

The oxidation of [Ni(mnt)$_2$]$^{2-}$ in the presence of benzo-15-crown-5 yields **70**. X-ray diffraction revealed that the dianions pack as columns and the counterions are discrete disodium triple-decker dications [73]. In contrast the stoichiometeric reaction of Na$_2$[mnt], NiCl$_2$ and benzo-15-crown-5 in CH$_3$OH–CH$_2$Cl$_2$ at r.t. leads to **71**. The structure of this complex reveals that the main segment comprises a chain structure, in which the [Ni(mnt)$_2$], lie in an end-to-end arrangements and interact with the Na crown units via CN···Na and S···Na contacts [74].

In a study by Schmauch et al. [75], [Co(mnt)$_2$]$^{2-}$ complexes were prepared with macrocyclic complex as the cation in a direct effort to produce magnetically interesting materials by introducing a planar cation that offers the direct possibility to interact with the paramagnetic [Co(mnt)$_2$]$^{2-}$ complex in the solid state. The complexes [M(tim)][Co(mnt)$_2$] **72** (Fig. 10) have been prepared in a straight forward manner by combination of the relevant salts in solution. Structural analysis of these isostructural salts shows that the [Co(mnt)$_2$]$^{2-}$ moiety is able to form stacks via the S atoms of the mnt above and below the central metal atom (S···Ni and S···Cu are 3.15 and 3.03 Å, respectively) ligated by the 2,3,9,10 - tetramethyl - 1,4,8,11 - tetraazacyclotetradeca-1,3,8,10-tetraene (tim) macrocycle. The magnetism of these complexes has been studied and it was found that the diamagnetic [Ni(tim)]$^{2+}$ induces antiferromagentic coupling of the [Co(mnt)$_2$]$^{2-}$, however, there is no coupling between the [Cu(tim)]$^{2+}$ and [Co(mnt)$_2$]$^{2-}$.

3.3. Open-shell counterions

These examples involve cations which themselves possess unpaired electrons or are capable of acting as electron donors. This provides a route to materials with novel physical properties where, for example, conducting and magnetic sublattices coexist. In addition, these systems often incorporate some rather unusual cations and, therefore, materials with new types of structure.

Construction of a material with, respectively, one and two paramagnetic components is achieved in the case of the complexes **73** and **74**. These salts contain the paramagnetic five-membered rings [PhCNSSN]$^+$ and [[*p*-ClC$_6$H$_4$–CNSSN]$^+$ in combination with anionic metal centres, which for **74** is also paramagnetic. Both anions and cations are essentially planar and in **74** the

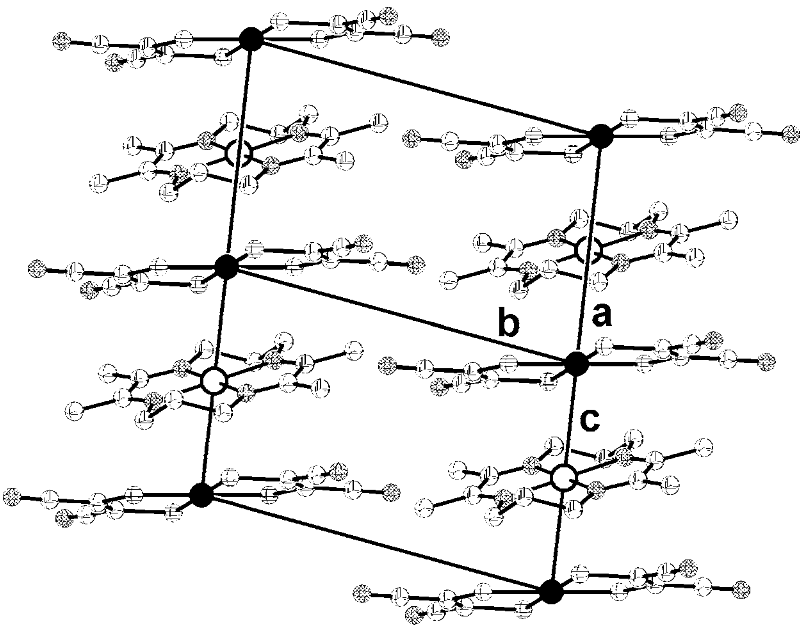


Fig. 10. A representation of the crystal structure of [Ni(tim)][Co(mnt)$_2$] **72**. The cobalt atoms are represented as black spheres, the nickel atoms by large open spheres, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres.

cations are arranged in pairs linked by a Cl^- ion via S···Cl contacts. In **73**, the cations are discrete and show mixed stacking with the anions [76].

A series of dipyridinium salts have been prepared of the form $\{A^{2+}[ML_2]^{2-}\}$ with M = Co, Ni; L = mnt [77] or M = Ni, Zn; L = mnt, dmit [78]. X-ray structural determination was achieved for [BQ][Co(mnt)$_2$] **75** and [A][Ni(mnt)$_2$] **76** where A = *trans*-4,4′-(1,2-ethenediyl)-bis[1-(3-cyanopropyl)pyridinium] however, electrical conductivities of these and the related salts were uniformly low.

Perhaps the most unusual structural types covered in this section are the structures of [NBu$_4$]$_2$[M(mnt)$_2$-Cu$_4$I$_4$], where M = Ni, Pd., Pt (**77**–**79**). In these structures the M(mnt)$_2$ moiety supports a novel eight-membered Cu$_4$I$_4$ via two cyano groups, four of which coordinate to two copper(I) ions in neighbouring molecules, resulting in the formation of a unique doubly-bridged one-dimensional (1-D) chain structure (Fig. 11).

Interestingly, a pressed pellet of [Ni(mnt)$_2$Cu$_4$I$_4$][NBu$_4$]$_2$, after exposure to iodine vapour for 7 days gave an electrical conductivity of 1.6×10^{-3} S cm^{-1} at r.t. although no further conclusions can be drawn from this due to any lack of structural information on the doped material.

3.4. TTF and perylene-based counter ions

In recent years, much effort has been aimed towards the preparation of materials that combine both magnetic and conducting sublattices. It is anticipated that such materials may lead to understanding of the influence of unpaired spins on the conductivity (or superconductivity) of the material and to novel magnetic coupling of the unpaired spins via the delocalised electrons. The ready availability of paramagnetic mnt complexes, and their tendency to form localised-electron systems with all but the smallest counterions, has led to these being attractive counterions for organic electron

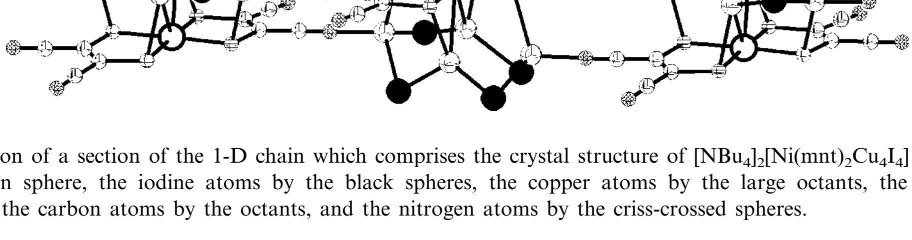


Fig. 11. A representation of a section of the 1-D chain which comprises the crystal structure of [NBu$_4$]$_2$[Ni(mnt)$_2$Cu$_4$I$_4$] **77**. The nickel atom is represented as an open sphere, the iodine atoms by the black spheres, the copper atoms by the large octants, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres.

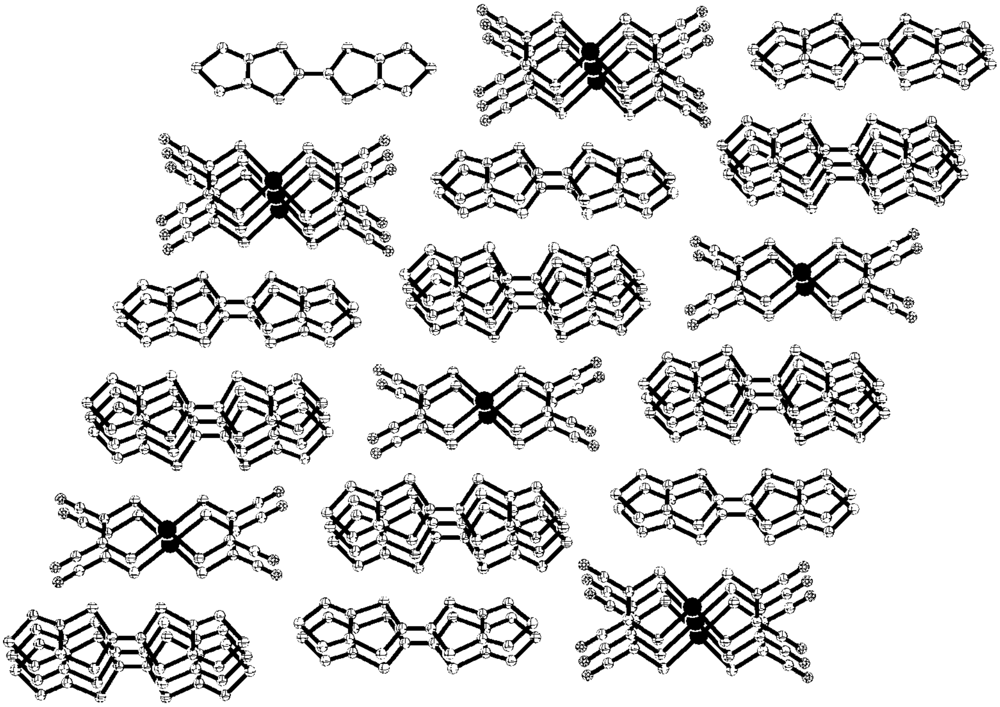


Fig. 12. A representation of the crystal structure of $[DT\text{-}TTF]_2[Au(mnt)_2]$ **77** looking down the crystallographic *b*-axis. The gold atom is represented as black spheres, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres.

donors such as TTF and perylene derivatives, capable of forming conducting molecular materials.

Electrocrystallisation of the π-electron donor dithiopheno-tetrathiafulvalene (DT-TTF) (Fig. 3(e)) with $[M(mnt)_2]^{X-}$ complexes gives rise to a family of radical ion salts $[DT\text{-}TTF]_2[M(mnt)_2]$ (**80**–**82**), which are isostructural and crystallise in the monoclinic space group $P2_1/n$ forming regular segregated stacks of donor and acceptor molecules along the *b*-axis (Fig. 12). The DT-TTF stacks are paired and interact strongly through S···S contacts in a ladder-like motif. The three salts have high r.t. electrical conductivities (40, 40 and 9 S cm^{-1} for **80**, **81** and **82**, respectively) but their conductivity temperature dependencies differ. The Au salt has an activated conductivity whereas the Ni and Pt salts are metal-like and both exhibit a metal-insulator transition around 120 K. Observation of a single line in their EPR spectra, which increases dramatically in width as the conductivity increases, is evidence for the presence of two magnetic subsystems which interact in the salts (M = Ni, Pt) with paramagnetic $[M(mnt)_2]^-$ ions [80,81].

These contrasting transport properties are accounted for by the differences in the transfer integrals along the DT-TTF stacks. The magnetic susceptibility of **82**, in which the $[Au(mnt)_2]^-$ anion is diamagnetic, can be fitted to a two-legged spin-ladder model. From diffuse X-ray scattering studies, it is established that below 220 K, the donors dimerise along the crystallographic *b*-axis and the spin carrier units in the ladder are identified as those formed by dimerised donors $[DT\text{-}TTF]_2^+$. In addition, zero-field and longitudinal field mu(+)SR measurements as a function of temperature on **82** have confirmed that this compound is a molecular material with a two-leg spin-ladder configuration. The results corroborate the theoretical expectations for the absence of magnetic order in even-leg spin ladders with the quantum spin-liquid state realised, despite the somewhat strong ladder–ladder interactions present [83].

Complexes **83** and **84** were prepared by electrocrystallisation of bis(ethylenethio)tetrathiafulvalene (BET-TTF) in the presence of $[NBu_4][M(mnt)_2]$, M = Au, Pt. The Au-containing salt **83** shows a mixed-stack arrangement with short S···S contacts between molecules in adjoining stacks. The salts were assigned as fully ionised from consideration of the optical and magnetic properties and hence contain diamagnetic metal complexes. The observed semiconductive behaviour of **83** is consistent with the structural arrangement and the fully ionised nature observed.

The Radical ion salt of 4-iodotetrathiafulvalene has been crystallised with $[Pd(mnt)_2]^{2-}$ and the resulting structure of the 1:2 salt **85** was found to form a mixed stack structure in which the $Pd(mnt)_2$ anions intermingle with pairs of 4-iodo-tetrathiafulvalene (ITTF) radical cations, i.e. a DDADDA stacking arrangement. The structure is characterised by short intermolecular contacts involving the iodine substituent interacting with the CN group of the complex [85]. This illustrates the capability of linear I···NC interactions to play a major role in the control of crystal architecture and suggests that other crystallisations of mnt complexes with I-bearing compounds can lead to good geometric control in magnetic or conducting materials.

Oxidised perylene-based units (Fig. 13(a)) are attractive cations for use in molecular materials with anions based upon mnt ligands, due to their planarity and large surface area, which, therefore, encourages favourable stacking interactions. This resulted in much early work combining these units with a variety of central metals in the mnt complex [[86] and refs. therein]. A thorough recent review of these salts has been conducted [87] in the context of other perylene-based conducting materials. The topic will, therefore, be dealt with only briefly here to indicate the variety of salts and properties displayed. Initially $[\mathrm{per}]_2[\mathrm{M(mnt)_2}]$ materials could be separated into Ni and Cu containing salts that display semiconductor behaviour (**87β**, **88β**) (β-phase) and Pt, Pd and Au containing salts that show metallic conduction (**89α**, **90α**, **91α**) (α-phase), however, α-phase salts of the Ni and Cu dithiolenes (**87α**, **88α**) were subsequently prepared [92]. Within this series, **89α** and **90α** represent unusual materials where localised unpaired spins on the mnt complex coexist with conducting chains formed by the perylene units. Much work in the past decade has, therefore, been aimed at a fuller understanding of these salts and their metal–insulator transitions.

Magnetic studies have been carried out to examine the magnetic-field dependence of the metal-to-insulator transition. In **89α**, it was found that the field dependence denotes the coupling of the Peierls transition in the perylene chains to a spin-Peierls-like transition in the $[\mathrm{Pt(mnt)_2}]^-$ chains, correlated with an anisotropic magnetic susceptibility, while **91α** gave a pure Peierls transition [90,91]. In an extension to this work experiments have been conducted which examine the properties of alloys of the $[\mathrm{Per}]_2[\mathrm{M(mnt)_2}]$ (M = Au and Pt) of the form $[\mathrm{Per}]_2[\mathrm{Au}_{1-x}\mathrm{Pt}_x(\mathrm{mnt})_2]$ [93]. In further studies on **87α**, magnetic susceptibility was dominated by a larger term due to the chains of $[\mathrm{Ni(mnt)_2}]^-$ spins, also vanishing at the metal to insulator transition (25 K). These results are compared with those of the other members of this family of compounds, and can be described as instabilities occurring in the conducting perylene chains (Peierls) and in the $[\mathrm{Ni(mnt)_2}]^-$ spin chains (spin-Peierls) [89].

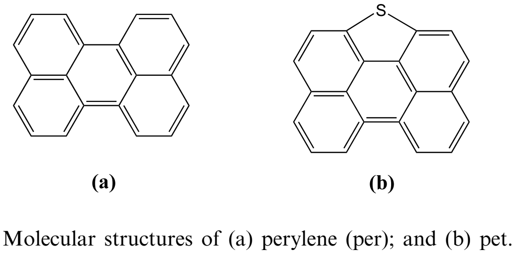


Fig. 13. Molecular structures of (a) perylene (per); and (b) pet.

In further studies, extending the range of available salts, **92** and **93** were prepared by electrocrystallisation. The crystal structure of **92** at r.t. consists of a close-packed arrangement of segregated stacks of perylene and $[\mathrm{Fe(mnt)_2}]$ components with dimerised $[\mathrm{Fe(mnt)_2}]_2$ units and thus differing from the structures of others in the series. The salts exhibit metallic behaviour down to 58 and 73 K, for **92** and **93**, respectively, where a metal–insulator transition occurs [95]. This is illustrated by X-ray intensity data showing a Peierls instability of the Perylene stacks. In contrast to other members of this series of two-chain compounds, the $\mathrm{M(mnt)_2}$ stacks can be considered to play no role in the Peierls instability [94,96].

Study of perylene-based conductors containing $[\mathrm{Co(mnt)_2}]^{X-}$ units has led to salts which differ in stoichiometry from others in the series. The 1:1 salt **94** was prepared and consists of almost regular perylene stacks and polymeric chains of dimerised Co-bis(dithiolate) units along the *a*-axis, with the solvent molecules disordered in the free spaces. Room temperature conductivity of 60 S cm^{-1} and absolute thermoelectric power of -8 μV K^{-1} suggest metallic behaviour at high temperatures. These transport properties and magnetic susceptibility measurements show a metal to insulator transition at 272–277 K and a second semiconductor-to-semiconductor phase transition at ca. 170–190 K [98]. Tight binding band structure calculations on **94** predict that the salt should be a 1-D metal with the conductivity originating from the perylene chains [97]. A unique 4:3 salt **95** was prepared as a by product of electrocrystallisation and contains the unusual trimer $[\mathrm{Co(mnt)_2}]_3$ with the overall formula suggested by EHMO calculations to be $[\mathrm{Co(mnt)_2}]_3^-[\mathrm{per}]_3^+[\mathrm{per}]^0$.

A different class of material was prepared using a modified perylene precursor perilo[1,12-*b*,*c*,*d*]thiophene (pet) (Fig. 13(b)), and **96** was obtained by electrocrystallisation from dichloromethane solutions of pet and $[\mathrm{NBu_4}][\mathrm{Ni(mnt)_2}]$. The crystal structure consists of segregated stacks along the *a*-axis of partially oxidised pet molecules arranged as trimers of $[\mathrm{pet}]_3^{2+}$ and dimerised $[\mathrm{Ni(mnt)_2}]_2^{2-}$ anions. The salt shows semiconductor behaviour with r.t. conductivity of ca. 9 S cm^{-1} with activation energy of 168 meV. Paramagnetic susceptibility is due to a singlet–triplet type contribution of antiferromagnetically coupled pairs of $S = 1/2$ spins of the $[\mathrm{Ni(mnt)_2}]^-$ species with $J/k_\mathrm{B} = -226$ K.

In conclusion, despite being known for three decades, $[\mathrm{M(mnt)_2}]^{X-}$ complexes are still playing a major role in the construction of magnetic and conducting molecular materials. In addition to the ease of preparation of complexes with various central metals, the planarity over the whole molecule can clearly be seen as an advantage in allowing close intermolecular interactions in comparison with many systems in Section 2 where bulky end-groups hindered close stacking. Although this can also prove a disadvantage in allowing easy dimerisation to give a diamagnetic ground state, the use of small and planar counterions has demonstrated that uniform stacking and more unusual packing motifs can be encouraged to overcome this. Only a few highly conducting systems where conductivity is through $[M(mnt)_2]^{X-}$ stacks have been prepared [7], mainly with alkali metal counterions and it seems apparent that these complexes have shown more utility in the preparation of magnetic materials and this has included ferromagnetic and spin-ladder systems. The latter illustrates the use of the metal complex as a diamagnetic unit in a passive packing role, taking advantage of the planarity that allows it to form the appropriate packing geometry with an organic electron donor. The structural characterisation of a ferromagnetic salt of $[Ni(mnt)_2]^-$ illustrates the opportunities to obtain structure–property relationships in functional salts of this nature. The combination of physical measurements and calculations has given some insight into the intermolecular interactions favourable for the realisation of ferromagnetic exchange. Future studies will no doubt continue to take advantage of these features but an opportunity may also exist to utilise the CN groups in more specific intermolecular interactions with iodine-bearing molecules in an attempt to design particular magnetic lattices as illustrated by the role of the iodine of ITTF in control of the structure of the salt with $[Pd(mnt)_2]^{2-}$.

4. $[M(bdt)_2]^{X-}$ and related complexes

Complexes of the form $[M(bdt)_2]^{X-}$ (Fig. 1(e)) and analogues have been studied in some detail since the 1960s [101,102] due to their preparation from readily available precursors and the recognition in them of the redox and spectral properties common to many metal bis-1,2-dithiolene families. Systematic use of these complexes in the preparation of magnetic and conducting materials, however, has not been undertaken in the way that families such as $[M(mnt)_2]^{X-}$ and $[M(dmit)_2]^{X-}$ have been widely exploited. This may be due to the perception of poorer intermolecular interactions for these in comparison with the $[M(dmit)_2]^{X-}$ class in particular owing to the reduced number of sulphurs in the $[M(bdt)_2]^{X-}$ complexes. In the last 15 years, however, these and structurally related analogues have been the subject of several studies highlighting the capability to form conducting or magnetic materials often using the basic benzene-1,2-dithiolate (bdt) unit as an element in a more extended delocalised ligand.

Similarities in structural and magnetic behaviour with the mnt analogue was highlighted by the complex $[NEt_4][Fe(bdt)_2]$ **97**, which has been structurally characterised and shows a dimer structure with the monomer units linked via intermolecular Fe···S contacts leading to antiferromagnetic coupling [103]. A series of related complexes were reported from toluene-1,2-dithiol of the form $[C]_x[M(S_2C_6H_3CH_3)_2]$ ($x = 2,1$) with M = Zn(II) (**98**) (C = NEt_4); Cu(II) (**99**), Ni(II) (**100**), Co(II) (**101**), Fe(II) (**102**) (C = NBu_4) and Mn(II) (**103**) (C = PPh_4) and were studied mainly for their eletrochemical and spectroscopic properties [104]. The X-ray structure of **102** was determined and again showed dimerisation of the complexes via a sulphur-over-Fe interaction. In a separate study [105,106], the structure of $[PPh_4]_2[Mn(S_2C_6H_3CH_3)_2]$ **103** was determined and showed an extremely distorted tetrahedral coordination geometry about Mn. Magnetic susceptibility measurements were consistent with high spin Mn(II).

Complexes containing multiple aromatic rings also received attention in the attempt to achieve high conductivity due to the extended delocalisation this can offer. The salt $[per]_2[Cu(qdt)_2]$ (**104**) (Fig. 14) was prepared by electrocrystallisation and the structure [107] consists of tetramerised stacks of perylene cations flanked by a centosymmetrically related pair of Cu complex anions. A charge of 1 − was assigned to each Cu complex by comparison of Cu–S distances with $[PPh_4]_2[Cu(qdt)_2]$ (**105**) and $[PPh_4][Cu(qdt)_2]$ (**106**). The structures of **105** and **106** were reported in a study of their spectroscopic and electrochemical properties [108], and a similar study has also been made of the analogous nickel complexes [109], although these were isolated only in diamagnetic oxidation states.

A series of salts [A][M(qdt)$_2$] was reported of formula A = BEDT-TTF, TMTSF, TTF, M = Au (**107**–**109**), Cu (**110**–**112**) and A = TTF, M = Ni (**113**) with r.t. conductivities ranging from 10^{-7} to 10^{-3} S cm^{-1} [110]. Conductivities in the series were much more sensitive to changes in the organic donor than the central metal in $[M(qdt)_2]^-$ suggesting this plays a more passive role as a counterion.

Related complexes have also been prepared containing terminal CN groups (**114**) (Fig. 15) as dianionic salts with $[NBu_4]^+$ counterions [111]. Charge-transfer salts with TTF were obtained by diffusion with $[TTF]_3[BF_4]_2$ in acetonitrile and show conductivities of the order 10^{-2}–10^{-3} S cm^{-1} at r.t.. The stoichiometry

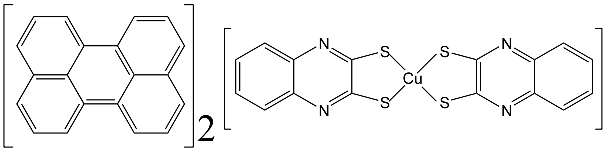


Fig. 14. Molecular structure of $[per]_2[Cu(qdt)_2]$, **104**.

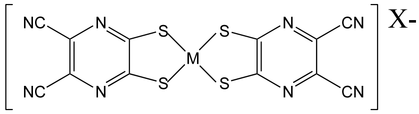


Fig. 15. Molecular structure of **114**, M = Ni, Pd.

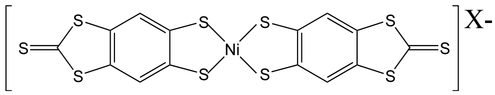


Fig. 16. Molecular structure of **115**, an extended analogue of [Ni(dmit)$_2$]$^-$.

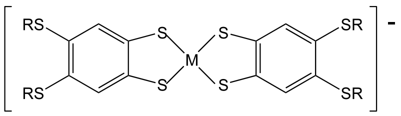


Fig. 17. M = Ni, Au; R = CH_3, $CH(CH_3)_2$, Me_2CH; RR = CH_2CH_2, >=O, >=S, CH_2SCH_2, CH_2.

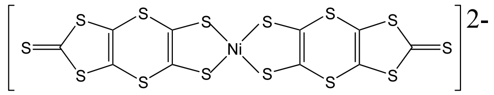


Fig. 18. Molecular structure of an extended analogue of [Ni(dmit)$_2$]$^-$.

was shown to be [TTF]$_5$[ML$_2$]$_2$ and the Pd complex was characterised by X-ray crystallography showing a stack of TTF molecules and a mixed stack containing a dimer of Pd complexes and another TTF. It is not clear if the Pd complex plays a significant role in contributing to the high conductivity of these salts. Further salts of these complexes with other organic electron donors have been reported [112].

An analogue of the [Ni(dmit)$_2$]$^{X-}$ complex has been reported with extended delocalisation via the inclusion of an aromatic ring in place of the C=C bond in the dmit complex (Fig. 16) [113–116].

The complex was isolated as [NBu$_4$]$_x$[NiL$_2$] (**115**) with $X = 2$, 1, 0.29 with the latter, non-integral salt, prepared by electrocrystallisation and showing metallic conductivity down to 20 K. The magnetic susceptibility of the 1:1 salt with radical metal complexes showed Curie–Weiss behaviour with a weak antiferromagnetic interaction. Other related complexes with Ni and Au were reported in the same studies and are shown in Figs. 17 and 18.

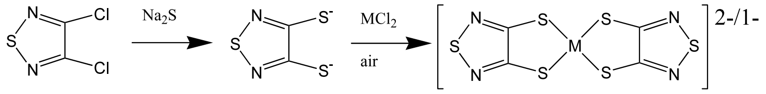
In such complexes, the difference between the first and second reduction potentials (2 − /1 − and 1 − /0) is taken as an estimate of the capability of the complex to delocalise charge, where a small difference is a desirable property for constructing molecular conductors. The values of this difference for complexes of the form **115** (Figs. 16 and 17) are larger than that of [Ni(dmit)$_2$]$^{X-}$ and as such would suggest that these are not as good candidates for molecular conductors. Further analysis of these complexes was also hampered by lack of structural data and further study involving these ligands was presumably impeded by lengthy preparation and difficulty in the use of low-solubility intermediates and precursors.

5. [M(tdas)$_2$]$^{X-}$

The first metal complexes of the ligand 1,2,5-thiadiazole-3,4-dithiol (tdas) were reported in 1990 and consisted of mono and dianionic nickel complexes (**116**, **117a**) with tetraphenylphosphonium or tetraalkylammonium counterions [117]. These were recognised as potential analogues of the [Ni(dmit)$_2$]$^{x-}$ species and are readily obtained in a one pot reaction from commercial precursors (Scheme 2).

A salt of composition [TTF]$_2$[Ni(tdas)$_2$] (**118**) was obtained by electrocrystallisation with a r.t. conductivity of 0.1 S cm^{-1} and indicated the potential of these complexes as components of conducting materials. The X-ray structure of the NEt$_4^+$ and NBu$_4^+$ dianionic salts (**117b**,**c**) [118] confirmed the planar geometry of these complexes and showed little interaction between metal complexes as expected for the diamagnetic dianionic species. The structure of the monoanionic salt **116** indicates a dimeric arrangement of the metal complexes [119] with a nickel-over-sulphur arrangement and a Ni···S distance of 2.385 Å. This interaction results in some deviation of the complex from planarity with a mean deviation of 0.2115 Å. Clearly this interaction occurs as a result of the unpaired electron present in the complex making intermolecular interaction favourable.

The salt [NBu$_4$][Fe(tdas)$_2$] **119** again shows a dimeric structure in the solid state (Fig. 19) [120] with an Fe···S distance of 2.501 Å. A detailed magnetic study of this salt was undertaken and showed behaviour typical of an antiferromagnetic dimer with susceptibility increasing with temperature. Two magnetic phase transitions were observed and the intradimer coupling constant J, in the range 190–240 K, showed a value around 10% larger than that above or below these temperatures. Recooling the sample showed hysteresis loops of width around 20 K for both these transitions. The data



Scheme 2. Preparation of [M(tdas)$_2$]$^{2-/1-}$.

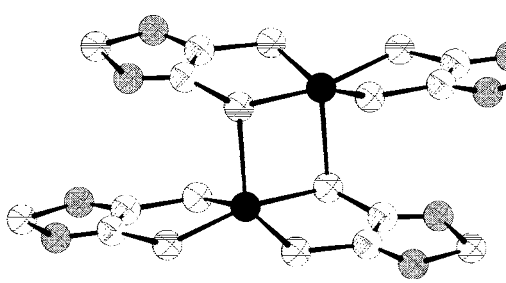


Fig. 19. A representation of the crystal structure of [TBA][Fe(tdas)$_2$] **119**. The iron atom is represented as black spheres, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by the criss-crossed spheres. The iron to sulphur distance is 2.501 Å. The cations are omitted for clarity.

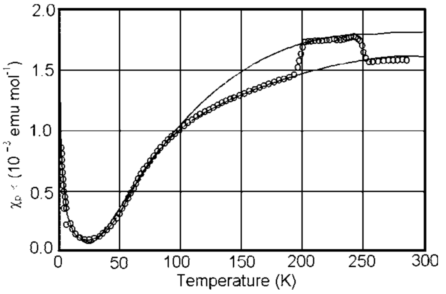
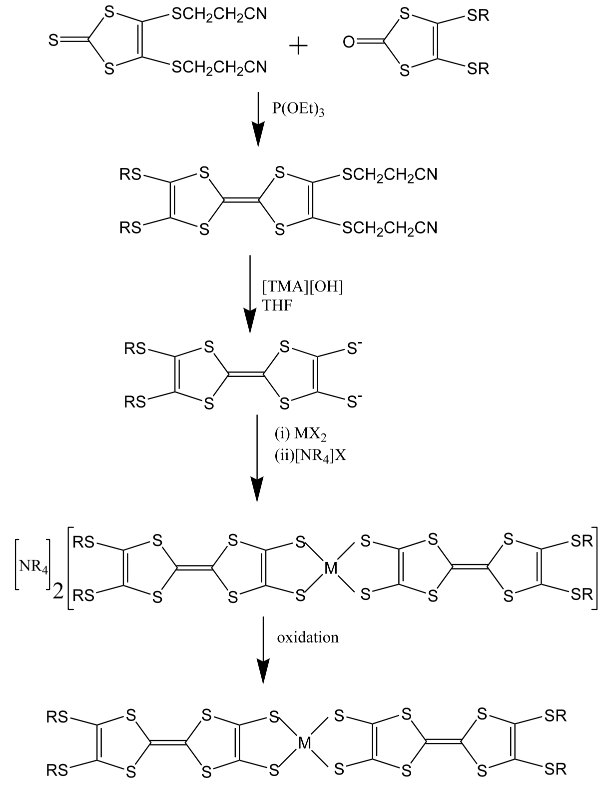


Fig. 20. Temperature-dependent magnetic susceptibility of [TBA][Fe(tdas)$_2$], showing re-entrant behaviour.



Scheme 3. Preparation of TTF-containing metal-bis-1,2-dithiolene complexes.

strongly suggested that the temperature dependence of the susceptibility can be explained as re-entrant behaviour (Fig. 20). The low temperature and high temperature phases are identical while an intermediate phase with a different structure exists between them. A Mossbauer study of the Fe complex in this salt indicated the Fe to have the intermediate spin state of 3/2 and that the change in magnetic properties is not associated with a change in spin state [121]. The tendency of [Fe(tdas)$_2$]$^-$ to dimerise was repeated in the semiconductive salt [TTF]$_2$[Fe(tdas)$_2$] (**120**) which also contains stacks of TTF molecules [122].

With the exception of the unusual magnetic data for **119**, [M(tdas)$_2$]$^-$ have generally proven unremarkable in their material properties. They have shown no preference to form conducting stacks and complexes with unpaired spins have shown a tendency to readily dimerise in a manner similar to [M(mnt)$_2$]$^-$ complexes which are also planar. If the ease of preparation and capability for strong intermolecular interactions are to be exploited, crystallisation with small or planar counterions to force materials away from the simple dimer geometry may be the most productive method forward.

6. Tetrathiafulvalene-dithiolene ligands

The incorporation of tetrathiafulvalene units into dithiolene ligands is appealing due to the superconductivity observed in several classes of salt containing TTF analogues. Thus, compounds that unite features of TTF species and metal dithiolene complexes were anticipated to offer enhanced intermolecular interactions and hence new conducting and magnetic behaviour. Tetrathiafulvalene compounds, which had been prepared as precursors for unsymmetrically-modified TTF species according to a general scheme involving phosphite mediated cross-coupling [123], were subsequently used as precursors to the TTF-containing dithiolene ligands (Scheme 3). Complexes studied are listed in Table 4.

The first complete characterisation of a metal complex containing such ligands including X-ray structure involved the dianionic mercury complex **121** [124] and showed an ca. tetrahedral geometry around the central metal leading to TTF components ca. perpendicular showing no significant interaction with each other. This was evidenced by cyclic voltammetry (CV) of the neutral analogue **123** that showed non-interacting unpaired electrons on the two TTF moieties. Significant deviations from planarity in the TTF units may be due to packing effects.

The first observation of high conductivity in neutral complexes containing these ligands was identified in the nickel complexes **124** and **125**, which displayed r.t. conductivity of 0.1 S cm^{-1} [125]. This can be compared with the conductivity of neutral [Ni(dmit)$_2$] which, although also unusually high at 3.5×10^{-3} S cm^{-1}, is two orders of magnitude lower than **124**, **125**. A typical neutral metal-bis-1,2-dithiolene material shows a conductivity around 10^{-5} or 10^{-6} S cm^{-1}. The X-ray structure of **125** indicated planarity in the complexes over the central nickel units and the TTF components, allowing extensive electronic delocalisation (Fig. 21). Stacking of the complexes with a perpendicular spacing of around 3.4 Å and side-by-side intermolecular interactions provide a pathway for conduction. The corresponding dianionic complexes isolated in this study **126**, **127** were highly air sensitive resulting in oxidation to the insoluble neutral species **125**, **128**. The complete absence of solubility of the latter in all common solvents combined with the difficulties of handling the dianions have proven problematic in the development of this area.

Nickel and copper complexes of the related ligand with a propylene group in place of the terminal alkyls have been prepared [126]. Monoanionic nickel complexes with PPh_4^+ and NMe_4^+ counterions (**129**, **130**) have been characterised by X-ray crystallography and represent the only examples of structurally charaterised monoanionic complexes in this class. Both structures show highly planar complexes and show stacking of the complexes with slippage of adjacent molecules along the long molecular axis by about one half of a molecular unit (Fig. 22(a and b)). The salt **130** showed additional short interactions along neighbouring chains, not present in **129** due to the larger counterion of the latter. The isolation of monoanionic salts of this complex contrast with the related complexes **124**–**128** where only highly sensitive dianionic and insoluble neutral complexes could be isolated despite attempts to prepare intermediate species by partial oxidation of the dianions. Electrical conductivity of **130** was found to be 1.4×10^{-3} S cm^{-1}, which again is high for a dithiolene complex with an integer oxidation state.

Table 4
Salts of metal-bis-1,2-dithiolene complexes with ligands containing TTF units

M	R	Charge	Cation		References
Hg	Et	2−	NMe_4	**121**	[124]
Hg	Bu	2−	NMe_4	**122**	[124]
Hg	Et	0	–	**123**	[124]
Ni	Me	0	–	**124**	[125]
Ni	Et	0	–	**125**	[125]
Ni	Et	2−	NMe_4	**126**	[125]
Ni	Bu	2−	NMe_4	**127**	[125]
Ni	Bu	0	–	**128**	[125]
Ni	$RR = CH_2CH_2CH_2$	1−	PPh_4	**129**	[126]
Ni	$RR = CH_2CH_2CH_2$	1−	NMe_4	**130**	[126]
Ni	$RR = CH_2CH_2CH_2$	0	–	**131**	[127]
Cu	$RR = CH_2CH_2CH_2$	0	–	**132**	[127]
Cu	$RR = CH_2CH_2CH_2$	2−	PPh_4	**133**	[126]
Cu	Me	0	–	**134**	[128]
Cu	Et	0	–	**135**	[128]
Cu	$RR = CH_2CH_2$	0	–	**136**	[128]
Pt	$C_{10}H_{21}$	2−	NBu_4	**137**	[129]
Pt	$C_{14}H_{29}$	2−	NBu_4	**138**	[129]
Pt	$C_{18}H_{37}$	2−	NBu_4	**139**	[129]
Pt	$C_{10}H_{21}$	0	–	**140**	[129]
Pt	$C_{14}H_{29}$	0	–	**141**	[129]
Pt	$C_{18}H_{37}$	0	–	**142**	[129]
Au	$RR = CH_2CH_2$	1−	NBu_4	**143**	[130]
Au	$RR = CH_2CH_2$	0.06−	NBu_4	**144**	[130]
Ni	$RR = CH_2CH_2$	1.5−	Na	**145**	[130]
Pt	$RR = CH_2CH_2$	0.4−	NBu_4	**146**	[130]
Ni	See Fig. 23			**147**	[131]

Recently, the neutral analogues, **131** and **132**, have been prepared and in the case of **131** structurally characterised. 1-D columns are formed along the *a*-axis, having short intrastack and interstack S···S contacts leading to a structural arrangement remarkably similar to **130** despite the difference in charge on the components. The conductivity of the crystal was found to be 7 S cm^{-1} at r.t. and showed semiconductor behaviour with an extremely low activation energy of 0.03 eV. High-pressure resistivity measurements up to 72 kbar, however, could not suppress the resistivity. The preparation of a metallic material, composed only of a single molecular component has long been a goal of work in the area of molecular conductors. The requirements for the preparation of such a material were discussed [127] in the context of these highly conducting single-component materials.

The related copper dianionic complex **133** was structurally characterised and shows a distorted tetrahedral geometry around the central copper with a dihedral angle of 54.2° between the ligands at the copper. The complexes again show a 1-D chain arrangement, with one of the TTF components of each molecule overlapping with one of the next. Magnetic susceptibility of this salt was interpreted in terms of a central Cu(II) ion which shows Curie behaviour indicating non-interacting spins.

Neutral copper complexes have been isolated with several terminal alkyl groups **134**–**136** [128]. Conductivity studies showed these complexes to be semiconductors with compressed pellet r.t. conductivities of 7.8×10^{-2}, 5.0×10^{-4} and 3.7 S cm^{-1}, respectively. The latter value represents an extremely high conductivity for an integral-oxidation-state salt in this family of complexes and for metal dithiolenes in general. Furthermore the large differences between complexes with different alkyl groups in the copper complexes **134**–**136** and in the nickel complexes **124**, **125** and **128** indicates the important role of the terminal alkyl groups in controlling the intermolecular interactions

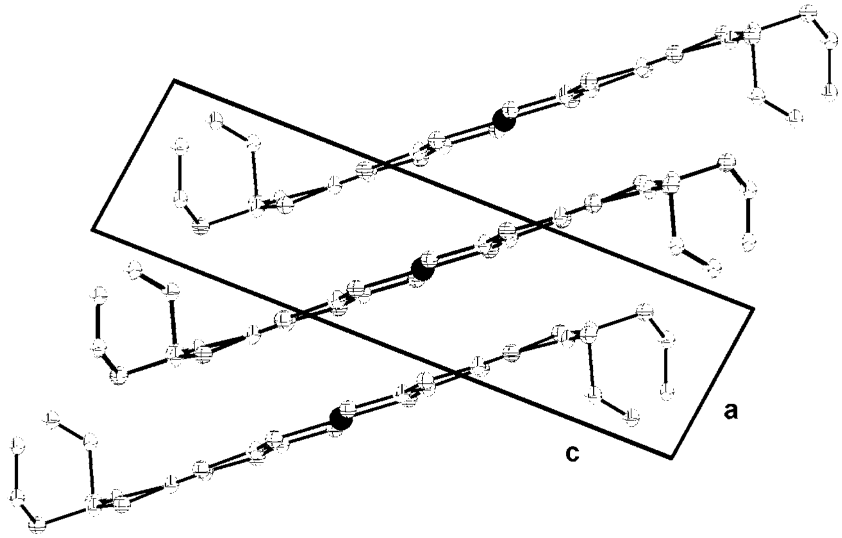


Fig. 21. A representation of the crystal structure of **125** showing stacking of the complexes. The nickel atom is represented by the black spheres, the sulphur atoms by the cross-hatched spheres and the carbon atoms by the octants.

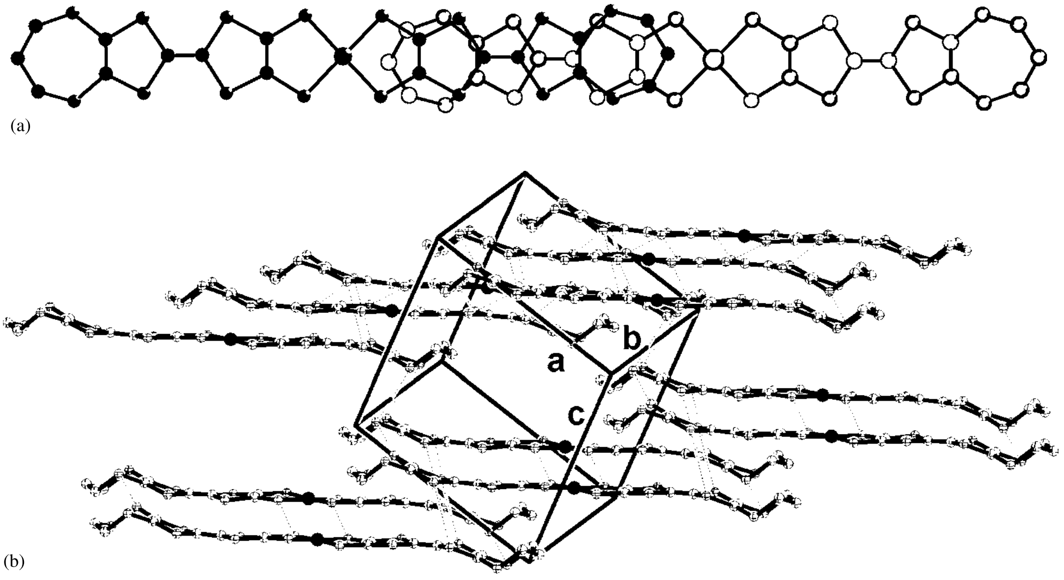


Fig. 22. (a) A representation of the crystal structure of **129**. This shows the stacking arrangements between individual molecules, the atoms forming the bottom molecule are shown by the open spheres whereas the atoms forming the top molecular are shown by the closed spheres. The cations are omitted for clarity. (b) A representation of the crystal structure of **130**. The nickel atom is represented by the black spheres, the sulphur atoms by the cross-hatched spheres and the carbon atoms by the octants. The short S···S interactions are shown by the dotted lines. The cations are omitted for clarity.

and hence the conducting properties. The magnetic susceptibilities of **134**–**136** were interpreted in terms of a central Cu(III) ion due to the small Curie constant for the temperature dependent component of the susceptibility corresponding to only 3.2% of that anticipated for Cu(II) ions. This suggests charge transfer to give an average charge of 1/2+ for each TTF unit and is manifested as a temperature independent component of the magnetic susceptibility. The presence of such a charge-transfer state is presumably the origin of the unusually high conductivity shown by these salts. Complexes **137**–**139** were prepared with long alkyl chain terminal groups, used to arrange the complexes in a layered structure via association of the long chains. In the X-ray structures of these salts no strong intermolecular interactions were observed due to the presence of the bulky cations, however, the neutral analogues **140**–**142** were prepared by oxidation and

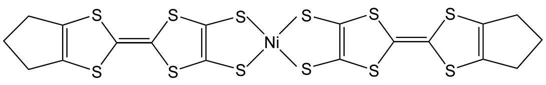


Fig. 23. Molecular structure of $[Ni(tmdt)_2]$, **147**.

showed high conductivities of around 10^{-2} S cm^{-1} for **140** and **141**.

A report of non-stoichiometric salts using extended ligands described preparation of Au **143**, **144**, Ni **145** and Pt **146** salts. These showed conductivities of 0.2–1.7 S cm^{-1}, however, no structural information was available to fully assess their properties.

Excitingly, the promise of a single-component metallic conductor has recently been realised in the neutral nickel complex **147** (Fig. 23). Single-crystal resistivity measurements showed $\sigma_{RT} = 400$ S cm^{-1} and metallic behaviour down to 0.6 K and the metallic nature of the solid was confirmed by magnetic susceptibility measurements. The behaviour was rationalised in terms of ab initio molecular orbital (MO) calculations that showed a small HOMO/LUMO energy separation. Subsequent tight-binding Extended Hueckel band structure calculations showed a 3-D Fermi surface when the HOMO/LUMO energy gap is assumed to be small.

Metal complexes of TTF-dithiolenes have shown the most promising conductivity properties of any dithiolene complexes except for those of dmit. The realisation of a single-component molecular metal has long been a synthetic target and has not been realised in any other molecular systems outside of dithiolene complexes. Low solubility of neutral species and air sensitivity have proven the main obstacles to progress in this area along with comparatively lengthy ligand preparation. Overall, however, remarkable results have been achieved, with suitable attention to these preparative methods, and this area promises to remain one of the most exciting within the field of metal-bis-1,2-dithiolene complexes.

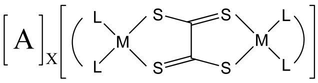


Fig. 24. Dinuclear species based on a tetrathiooxalate bridge (Table 5).

7. Multimetallic species

Much work in the preparation of new dithiolene-containing molecules has focused towards extending the delocalisation of the complex to reduce on-site coulomb repulsions, increase the possibility of intermolecular interactions and, in the case of optical materials, to achieve lower energy absorptions. As an alternative to lengthy organic synthetic procedures aimed at new, extended ligands, compounds containing more than one metal centre can offer an alternative strategy to prepare such systems. Additionally, multimetallic species can provide model systems to explore the intramolecular metal–metal magnetic interaction mediated by selected bridging ligands.

Within this context, a series of complexes based on dinuclear systems containing a tetrathiaoxalate bridge has been explored (Fig. 24) including structural characterisation (Table 5).

Deliberate preparation of these complexes largely depends upon a simultaneous reaction between $C_2S_4^{2-}$, M^{2+} and $L^\wedge L^{2-}$ in the presence of the appropriate counterion. Formation of the product is thus in competition with formation of insoluble $[M(C_2S_4)]_n$ and $[M(L^\wedge L)_2]^{2-}$ and typical yields can be 14–30% for the Cu complexes and 30–40% for the Ni complexes. The isolation of several analogous complexes and salts in both the Cu and the Ni series suggests that, despite the difficulties expected in obtaining the desired product from such a mixture, reproducible methods in acceptable yield are available. Additionally, a higher yielding

Table 5
Salts of dinuclear complexes based on a tetrathiooxalate bridge

M	$L^\wedge L$	Charge (*X*)	Cation (A)		References
Cu	dmid	2−	$AsPh_4$	**148**	[134]
Cu	dmit	2−	NBu_4	**149**	[135]
Cu	mnt	2−	NBu_4	**150**	[136]
Cu	dsit	2−	NBu_4	**151**	[136]
Cu	dmid	2−	NBu_4	**152**	[136]
Ni	$S_2C_2S_2C_2(CO_2Me)_2$	2−	$AsPh_4$	**153**	[137]
Ni	$S_2C_2S_2C_2(CO_2Me)_2$	0	NBu_4	**154**	[137]
Ni	dmit	2−	NBu_4	**155**	[138,132]
Ni	dmit	2−	$(Ph_3P)_2N$	**156**	[133]
Ni	dsit	2−	NBu_4	**157**	[139]
Ni	dmise	2−	NBu_4	**158**	[139]
Ni	dmit	2−	NMe_4	**159**	[139]
Ni	dmit	2−	NEt_4	**160**	[139,140]
Ni	dmid	2−	NBu_4	**161**	[141]

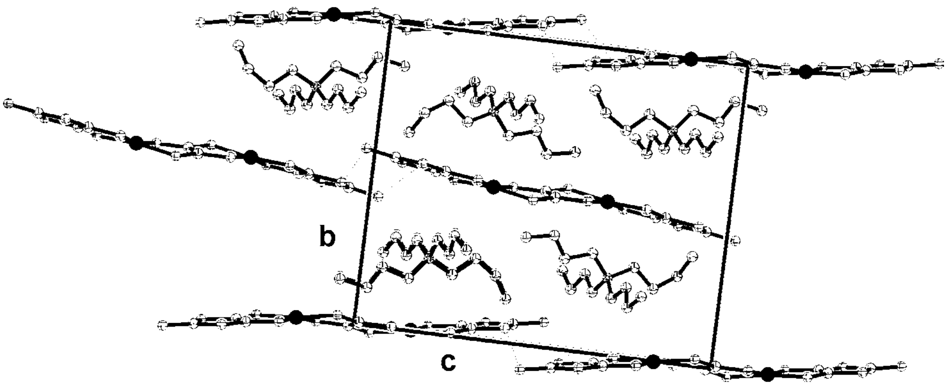


Fig. 25. A representation of the crystal structure of **149**. The Cu atom is represented by the black spheres, the sulphur atoms by the cross-hatched spheres and the carbon atoms by the octants.

alternative route for **155** has been reported [132] and an accidental preparation of **156** [133].

The X-ray structures of the Cu complexes **148**–**152** all show a C–C distance within the C_2S_4 unit comparable with that of the dianion $C_2S_4^{2-}$ and that the $Cu(C_2S_4)Cu$ core is essentially planar. These complexes are thus best formulated as containing Cu(II) with two terminal and one bridging dianionic ligand. The 1,2-dithiolene ligands generally show a tetrahedral distortion with respect to this core with dihedral angles around 18.87–28.3° and only **150** showing a planar structure with dihedral angle of 0°.

Complex **149** packs with sheets of anion chains forming head-to-tail contacts with a short intermolecular S···S interaction of 3.634 Å (Fig. 25). A similar packing scheme is displayed by **151** with the structurally related $C_3Se_2S_3$ ligand able to form an analogous intermolecular interaction. In contrast, complex **150** shows a structure composed of isolated anions, in keeping with the reduced ability of mnt to form intermolecular contacts.

In the case of the Ni complexes **153** and **155**–**161**, a planar $Ni(C_2S_4)Ni$ core is also observed but with a central C–C bond typically around 1.43 Å in contrast to a typical value of around 1.48 Å for the Cu analogues. This has been interpreted as intermediate between $C_2S_4^{2-}$ and $C_2S_4^{4-}$ with Ni intermediate between Ni(II) and Ni(III). The Ni complexes are not completely planar, but show dihedral angles between the C_2S_4 unit and the 1,2-dithiolene unit between 3.6 and 24.5° leading to a chair-type conformation. Clearly, the counterion plays a crucial role in this distortion as evidenced by angles of 3.6° for **159** and 24.5° for **160**. Tetrahedral-type distortions analogous to the Cu complexes were not observed. For **161**, conducting salts have been obtained with organic donors TTF and BEDT-TTF.

Salts **155**–**158** possess 1 or 2-D sheets of anions where intermolecular interactions are formed via the non-coordinating S and Se atoms of the complexes and are thus reminiscent of Cu complexes **149** and **151**. Salt **159**, however, with the smaller $[NMe_4]^+$ counterion shows much more extensive intermolecular S···S interactions with face-to-face stacking of the complexes (Fig. 26).

CV revealed for **155**–**158** a reversible oxidation to the monoanion at −0.82 to −0.83V followed by an irreversible process at −0.15 to −0.23 V (vs. Ag/AgCl) associated with the deposition of non-integer material on the electrode. This behaviour is closely related to that of salts such as $[Ni(dmit)_2]^{2-}$ capable of forming molecular metals and suggests these extended complexes may be able to form analogous species. The Cu complexes **149**–**152** show two reversible redox processes with the first reduction at −0.63 to −0.79 V and the second at 0.00 to −0.15V. These are assigned as reduction to the monoanionic and to the neutral species, respectively.

Study of the magnetic properties of **148** revealed a very strong antiferromagnetic coupling between the $S = 1/2$ Cu(II) centres mediated via the dithiooxalate bridge with $|J| > 800$ cm^{-1}. Attempts have been made to prepare electrically conducting materials from these building blocks by electrocrystallisation, slow interdiffusion and chemical oxidation and a series of non-integral salts of $[(dmit)Ni(C_2S_4)Ni(dmit)]$ and the Cu analogue with TTF and $[NBu_4]^+$ counterions has been obtained [135,139]. Conductivities of these range from 0.01 to 0.5 S cm^{-1} but study to date has not yielded any structural data to help rationalise these results.

A series of papers has reported the preparation, structural, optical and electrochemical properties of a range of complexes derived from porphyrazines, functionalised around the periphery with bis-1,2-dithiolene chelating units (Fig. 27). Early reports concerned the symmetrical octa-thia system which was shown to be able to externally coordinate SnR_2 units via two S^- and one N in a tridentate mode [142,143] in addition to the expected five-membered 1,2-dithiolene chelate to metal bis-phosphine units [144]. Subsequently, porphyrazines bearing 1-3 dithiolene substituents were prepared with the remaining positions occupied by fused benzene rings analogous to a phthalocyanine [145–147] or by

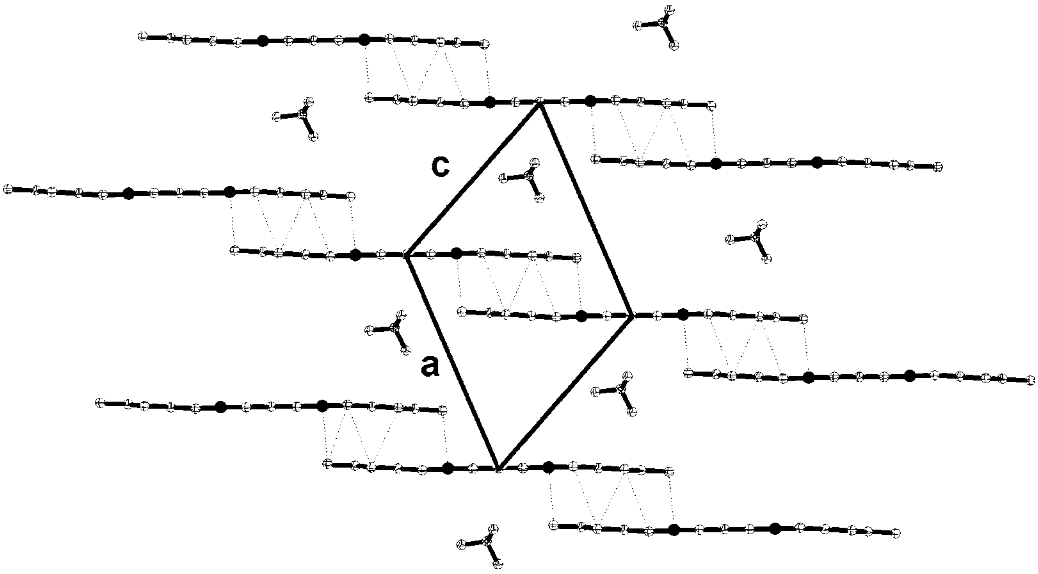


Fig. 26. A representation of the crystal structure of **159**. The nickel atom is represented by the black spheres, the sulphur atoms by the cross-hatched spheres and the carbon atoms by the octants. The smaller cations allow the S···S interactions which can be seen by the dotted lines.

$R = p$-$(C_6H_4)CH_3$ groups to aid solubility [148]. Related species bearing amino groups in place of the S^- group were also isolated [149]. These latter species have been used to prepare a range of symmetric and asymmetric bis-1,2-dithiolenes (Fig. 28) and mixed 1,2-dithiolene-1,2-diamino complexes.

Complexes families studied included $[Ni(L^1)_2]$, and $[M(X)(Y)]$ where M = Pd(II), Pt(II); $X = L^2$, L^3, L^4 and $Y = mnt^{2-}$, 2-oxo-1,3-dithiole-4,5-dithiolate ($dmid^{2-}$), bdt^{2-}, $dmit^{2-}$ (**162**) and also [(X)M(Y)M(X)] where, M = Pd(II), $X = L^2$, L^3, L^4 and H_4Y = 1,2,4,5,benzenetetrathiol (**163**). Studies on these complexes to date have focused mainly on synthetic strategy, optical and redox properties, however, the realisation of extended π-systems incorporating elements of both 1,2-dithiolene complexes and phthalocyanines, both of which are utilised in the formation of high conductivity materials, suggests that the exploitation of these complexes in this area would prove fruitful. Furthermore, the opportunity to use these systems to link paramagnetic metal centres in multimetallic species or in chains has been recognised [148] and is also likely to lead to novel systems for magnetic studies.

Two complexes have been reported [150] containing a dithiol-bridged Ni_5 and Ni_3 chain, respectively, terminated by $dmit^{2-}$ ligands of formula $[NEt_4]_2[Ni_5(edt)_4(dmit)_2]$ (**164**) and $[AsPh_4]_2[Ni_3(pdt)_2(dmit)_2]$0.5 MeOH (**165**). Both complexes were structurally characterised and show ca. square–planar coordination for all Ni atoms. Complex **164** is centosymmetric but in **165**, a V-shaped arrangement of the Ni atoms is adopted. Pressed-pellet electrical conductivities of the complexes were 1.52×10^{-5} and 1.75×10^{-4} S cm^{-1}, which compares favourably with other integral oxidation state metal-dithiolene complexes.

Complexes in the families discussed in this section have so far been studied mainly in the context of their synthetic realisation and molecular properties including electrochemistry. It is apparent that many of these possess features characteristic of other classes of compound capable of forming conducting or magnetic

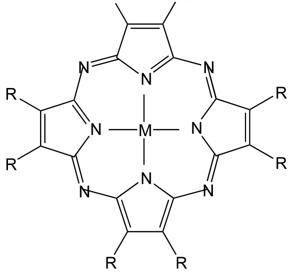


Fig. 27. M = Cu, Ni; $R = S^-$ or RR = fused benzene ring.

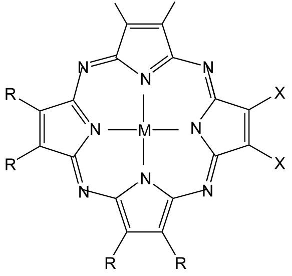


Fig. 28. L^1, $M = Ni^{II}$, $R = p(C_6H_4)CH_3$, $X = S^-$; L^2, $M = Ni^{II}$, $R = C_3H_7$, $X = NH_2$; L^3, $M = Cu^{II}$, $R = C_3H_7$, $X = NH_2$ L^4, $M = Mn^{III}$, $R = C_3H_7$, $X = NH_2$.

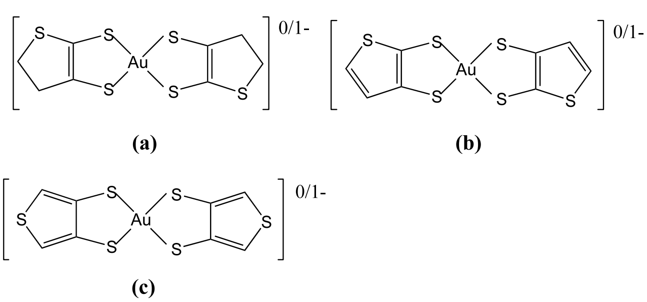


Fig. 29. Molecular structures of the monoanions **166** (a), **167** (b) and **168** (c) and the neutral species **169** (a) **170** (b) and **171** (c).

molecular materials including several reversible redox steps, stable paramagnetic species, a high degree of planarity and metal or sulphur atoms suitable for intermolecular contacts. In addition, the presence of more than one metal atom distinguishes these from other families of complexes and offers possibilities of unexpected new features. It remains to be seen whether these properties will be exploited in the preparation of materials. Initial results yielding conducting materials derived from **159** for example, are promising but will require structural data for progress to be made.

8. Miscellaneous complexes

Recently, the first report was made of transition metal complexes with dithiothiophene ligands [151] (Fig. 29) as both monoanionic and the corresponding neutral gold complexes **166**–**171**. Although the X-ray structures of the monoanionic **166** and **168** were obtained, the neutral complexes showed low solubility and suitable crystals could not be grown. The r.t. conductivity of compressed pellets of **169**–**171** was measured and that of **170** was shown to be remarkably high at 6 S cm^{-1}. Furthermore, both the magnetic susceptibility and thermopower data for this material were consistent with metallic conductivity. Although, electrical conductivity decreases with decreasing temperature, it was suggested that this is due to interparticle resistance within the compressed pellet and that the intrinsic behaviour of the material is metallic. Thus, this appears to be a single-component metallic conductor, a phenomenon until recently unknown in any class of molecular conductor. The only other example of such a material was also recently discovered, is also a metal-bis-1,2-dithiolene complex, and is discussed in Section 6.

Complexes of the formula $[\mathrm{M(tfd)_2}]^{X-}$ have been studied for several decades and older examples are discussed in a previous review [8]. Few of these involve structural characterisation where paramagnetic complexes or other paramagnetic or conducting components are incorporated. Examples that have been explored include salts with perylene and pyrene showing little charge transfer, and also essentially ionic salts with tropylium, phenothiazene, phenoxazine [8] and more recently hexaazaoctadecahydrocoronene [152]. In general, the multiple fluorine atoms result in comparatively electronegative complexes and, therefore, complete charge transfer with organic electron donors. In addition the limited electronic delocalisation over the complexes and the non-planar end groups reduces the opportunity for strong intermolecular interactions.

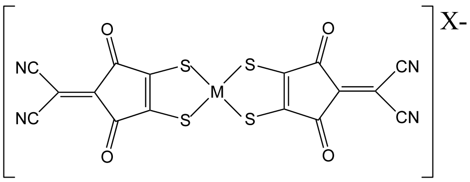
Structural investigations of complexes containing phenyl groups attached to the metal-bis-1,2-dithiolene core include $[\mathrm{NBu_4}][\mathrm{Pt(S_2C_2Ph_2)_2}]$ (**172**) [153], $[\mathrm{MV}][\mathrm{Ni(S_2C_2Ph_2)_2}]_2$ (**173**) [154] and $[\mathrm{NBu_4}][\mathrm{Ni(S_2C_2Ph_2)_2}]$ (**174**) [155]. These reveal that the phenyl rings can deviate from the plane of the square–planar complex by up to 76°. Little information on conductivity or magnetism for such complexes has been reported.

The structural characterisation of $[\mathrm{M(S_2C_2(CO_2Me)_2)_2}]^-$ has been achieved for M = Ni, Fe (**175**, **176**) with the Fe [156] complex showing a dimer arrangement analogous to $[\mathrm{FeL_2}]^-$ systems with L = mnt, tdas and bis(trifluoromethyl)ethylenedithiolate (tfd). Complex **175** [157] was crystallised as the $[\mathrm{AsPh_4}]^+$ salt and shows non-stacked metal complexes, well separated and nearly orthogonal. This leads to little intermolecular interaction as evidenced by magnetic susceptibility measurements.

Functionalised dithiooxamides have been used to achieve discrete, non-polymeric bis-1,2-dithiolene complexes, however, the majority of these contain Ni(II), Pd(II) or Pt(II) centres and are diamagnetic. The paramagnetic complex $[\mathrm{Cu(S_2C_2(NHCHPh)_2)_2}]^{2+}$ (**177**) has been structurally characterised [158] but no particular study was made of the magnetic properties. A related ligand, however, was used to prepare a trinuclear Cu(II) species (**178**) [159]. In this species, the dithiooxamide ligand has been extended to give $\mathrm{S_2C_2(NHC_3H_6SH)_2}$ whereby two additional Cu(II) centres have been coordinated via the pendant thiol-bearing arms and the deprotonated amides and thus form a planar $\mathrm{Cu(II)(N_2C_2S_2)Cu(II)(S_2C_2N_2)Cu(II)}$ core as shown by X-ray structural analysis. Detailed magnetic studies were carried out on **178** and showed $J = -483$ cm^{-1} between adjacent Cu(II) centres with coupling between the outer two assumed to be zero. Related species were reported with pendant alcohol groups in place of the thiols and with Ni(II) in place of the three Cu(II) centres.

Complexes containing ketone groups adjacent to the C=C group have been prepared and structurally characterised (Fig. 30).

The complex **179** with M = Cu and $X = 2-$ [160] has been shown to consist of weakly coupled dimers



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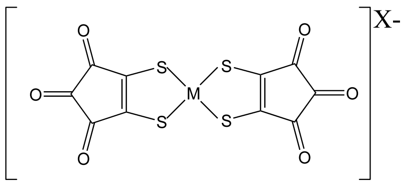

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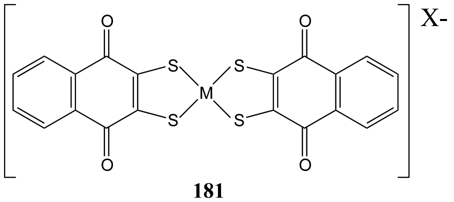

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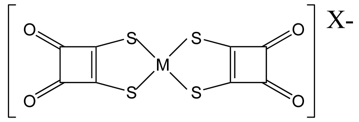


182

Fig. 30. Molecular structure of complexes containing ketone groups adjacent to the C=C, **179**–**182**.

which obey the Bleaney–Bowers expression with a coupling constant of $2J = 12$ cm^{-1}. The complexes were shown to be non-planar with a dihedral angle between ligands of 36.76°, not untypical of other Cu(bis-1,2-dithiolene) complexes. The related diamagnetic examples of **179** and **180** with M = Ni, Pd and Pt and $X = 2-$ were reported. Paramagnetic, monoanionic complexes of all these could be generated in solution by chemical or electrochemical oxidation [161], however, attempts at isolation were unsuccessful.

Preparation and X-ray structures have been reported [162] for complexes of naphthoquinonedithiolate (nqdt) with metals Fe, Cu, Ni, Pd, Co and Mn (**181**). The monoanionic Ni complex has been structurally characterised as the $[NBu_4]^+$ salt, and this showed the planar complexes to be well separated by the large counterions (Fig. 31). Despite this, a weak ferromagnetic transition at 4.43 K is reported accompanied by weak hysteresis below this temperature. The corresponding Cu complex is isomorphous and despite having an even electron count is paramagnetic at r.t., the material becoming diamagnetic at 6 K. This is interpreted as a low-lying thermally populated triplet state.

The complex **181** with M = Co, has been structurally characterised and shows a dimeric metal-over-sulphur arrangement of the complexes, with no short intermolecular contacts between dimers. The observation of high temperature paramagnetism in this complex is consistent with two independent electrons per dimer and obeys the Curie–Weiss law to 20 K where the susceptibility becomes larger than predicted. This behaviour is interpreted in the light of calculations that show ca. degenerate HOMO orbitals, containing two electrons. $[NBu_4][Mn(nqdt)_2]$ has not been structurally characterised but calculations suggest a tetrahedral metal environment. As the temperature is lowered there is an increase in magnetic susceptibility corresponding to a weak ferromagnetic transition at 40 K attributed to a spin canting mechanism.

Clearly, the $[M(nqdt)_2]^{X-}$ complexes (**181**) represent an unusual class of materials and this can probably be attributed to the redox-active nature of the ligand in addition to the central dithiolene core. This is reminiscent of the TTF-containing dithiolenes (Section 6) where the possibility of intramolecular electron transfer was noted in the context of highly conducting undoped molecular materials. This again emphasises that further studies of these or other planar metal dithiolene complexes containing redox-active ligands are likely to generate new and unexpected magnetic and conducting behaviour such as the weak ferromagnetism observed in $[NBu_4][Ni(nqdt)_2]$.

The dithiosquarate complex **182** with M = Pt has been used as a component in structurally-characterised salts with electron donor organic compounds to give $[\text{BEDT-TTF}]_2[Pt(S_2C_4O_2)_2]$ [163]. The structure of this species contains mixed stacks of $[\text{BEDT-TTF}^+]_2$ dimers and $[Pt(S_2C_4O_2]^{2-}$ anions leading to diamagnetic behaviour. Related salts with TTF donors have been reported [164] including structural characterisation of $[TTF]_2[Pd(S_2C_4O_2)_2]$ and $[TTF]_3[Pt(S_2C_4O_2)_2]$. These also both contain dimerised $[TTF^+]_2$ units with the latter containing an independent, neutral TTF perpendicular to the dimer. This leads to high resistivity in these and related salts $[TTF]_2[Pt(S_2C_4O_2)_2]$ and $[TTF][Cu(S_2C_4O_2)_2]$.

An analoguous ligand to mnt has been prepared with one of the CN groups replaced by H [165]. The synthesis and X-ray structure was reported for $[PPh_4]_X[Ni(S_2C_2(H)CN)_2]$ **183**, $X = 1,2$. The monoanionic species was dimeric in the solid state and a singlet ground state was observed by magnetic susceptibility measurement. A similar species has been prepared with a 1,3-dithiole-2-one five-membered ring in place of the CN group in **183**. Thus, the preparation and X-ray structure was reported for $[NBu_4][Ni(S_2C_2(H)(C_2HS_2CO))_2]$ **184** [166].

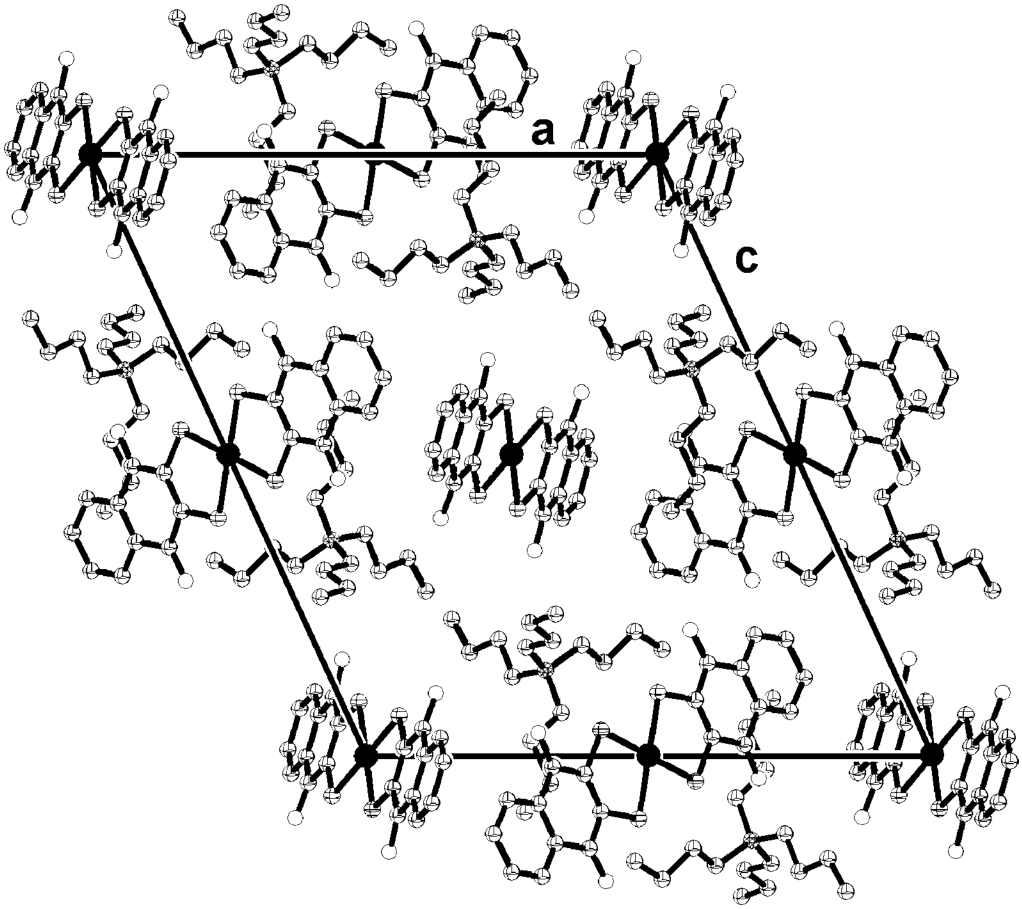


Fig. 31. A representation of the crystal structure of **181**. The nickel atom is represented by the black spheres, the sulphur atoms by the cross-hatched spheres, the oxygen atoms by the empty spheres, and the carbon atoms by the octants.

Unsymmetrical metal bis-1,2-dithiolene complexes have been seldom reported, despite the obvious use of this approach to greatly extend the number of complexes available for study. A series of unsymmetrical Ni complexes containing ligands such as dmit, mnt and dddt has been reported [167] including some structural characterisation. These were prepared by ligand exchange of two symmetrical complexes followed by chromatographic separation. Electrochemical studies suggest these salts show additive properties of the two ligands and preliminary electrocrystallisation studies yielded metallic conducting salts [TTF][Ni(dmit)(mnt)] (**185**) and [Ethylenedithiotetrathiafulvalene (EDT-TTF)][Ni(dmit)(mnt)] (**186**).

9. Metal-bis-1,2-dithiolene complex salts containing metallocenes

In the preparation of molecular magnetic materials, metallocene containing materials have often been studied due to the ability of spin carrying metallocene complexes to participate in intermolecular interactions and hence long-range magnetic ordering. This has been typified by donor–acceptor salts, such as [FeCp$_2^*$][TCNE] and related species using other metallocenes or other organic electron acceptors. Although not specifically discussed here, this larger family of salts involving organic electron acceptors have shown interesting properties including ferromagnetism [168].

An attractive material type, therefore, has been the use of metal-bis-1,2-dithiolene anions in such salts in place of the organic electron acceptor to create donor–acceptor salts where both components can contribute to the bulk magnetic behaviour and can be varied to modify the material properties. Preparation of such salts is normally achieved by a straightforward metathesis process by mixing [Metallocene]$^+$X$^-$ with A$^+$[metal-bis-1,2-dithiolene]$^-$ in a suitable solvent to precipitate the desired product. Growth of high quality single crystals can be more difficult, but is often achieved by slow inter-diffusion of the same precursors.

A large number of salts of this class have now been prepared and are summarised in Table 6. This has led to a host of different packing motifs and different magnetic behaviours ranging from Curie paramagnets to metamagnets and ferromagnets.

Table 6
Salts containing metallocene cations and metal-bis-1,2-dithiolene complex anions

Metallocene	Dithiolene	Solvent	Ratio		References
$[Fe(cp^*)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**187**	[169]
$[Fe(cp^*)_2]^+$	$[Pt(mnt)_2]^-$	–	1:1	**188α**, **188β**	[169]
$[Fe(cp^*)_2]^+$	$[Co(mnt)_2]^-$	CH_3CN	1:1:2	**189**	[170]
$[Fe(cp^*)_2]^+$	$[Fe(mnt)_2]^-$	CH_3CN	1:1:2	**190**	[170]
$[Fe(cp^*)_2]^+$	$[Co(mnt)_2]^-$	–		**191**	[170]
$[Fe(cp^*)_2]^+$	$[Cu(mnt)_2]^{2-}$	–	2:1	**192**	[170]
$[FeCp_2]^{+/0}$	$[Ni(mnt)_2]^-$	–	3:2	**193**	[171]
$[Fe(C_5H_4R^1)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**194**	[172]
$[Fe(C_5H_4R^2)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**195**	[172]
$[Fe(C_5H_4R^3)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**196**	[172]
$[Fe(C_5H_4R^4)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**197**	[172]
$[Fe(C_5Me_4SMe)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**198**	[173]
$[Fe(C_5Me_4SMe)_2]^+$	$[Pt(mnt)_2]^-$	–	1:1	**199**	[173]
$[Fe(C_5Me_4SMe)_2]^+$	$[Co(mnt)_2]^-$	–	1:1	**200**	[173]
$[Fe(C_5Me_4S^tBu)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**201**	[173]
$[Fe(C_5Me_4S^tBu)_2]^+$	$[Pt(mnt)_2]^-$	–	1:1	**202**	[173]
$[Fe(C_5Me_4S^tBu)_2]^+$	$[Co(mnt)_2]^-$	–	1:1	**203**	[173]
$[Fe(C_5HMe_3S^tBu)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**204**	[174]
$[Fe(C_5HMe_3S^tBu)_2]^+$	$[Pt(mnt)_2]^-$	–	1:1	**205**	[174]
$[Fe(C_5Me_4S)_2S]^+$	$[Ni(mnt)_2]^-$	–	1:1	**206**	[174]
$[Fe(C_5Me_4S)_2S]^+$	$[Pt(mnt)_2]^-$	–	1:1	**207**	[174]
$[Fe(C_5H_2Me_3)(C_5HMe_3R]^+$	$[Ni(mnt)_2]^-$	CH_2ClCH_2Cl	1:1:1	**208**	[174]
$[Fe(C_5H_4R^5)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**209**	[174]
$[Fe(C_5H_4R^5)_2]^+$	$[Ni(mnt)_2]^-$	CH_2ClCH_2Cl	1:1:1	**210**	[174]
$[Fe(C_5H_4R^5)_2]^+$	$[Pt(mnt)_2]^-$	–	1:1	**211**	[174]
$[Fe(C_5H_4R^6)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**212**	[174]
$[Fe(C_5H_4CH_2NMe_3)_2]^+$	$[Ni(mnt)_2]^-$	–	1:1	**213**	[175,176]
$[Fe(C_5H_4CH_2NMe_3)_2]^+$	$[Pt(mnt)_2]^-$	–	1:1	**214**	[175,176]
$[Fe(C_5H_4CH_2NMe_3)_2]^+$	$[Cu(mnt)_2]^-$	–	2:1	**215**	[176]
$[Fe(cp^*)_2]^+$	$[Ni(tfd)_2]^-$	–	1:1	**216**	[169]
$[Mn(cp)_2^*]^+$	$[Ni(tfd)_2]^-$	–	1:1	**217**	[177]
$[Mn(cp)_2^*]^+$	$[Pd(tfd)_2]^-$	–	1:1	**218**	[177]
$[MnCp_2^*]^+$	$[Pt(tfd)_2]^-$	–	1:1	**219**	[177]
$[CrCp_2^*]^+$	$[Ni(edt)_2]^-$	–	1:1	**220**	[178]
$[FeCp_2^*]^+$	$[Ni(edt)_2]^-$		1:1	**221**	[178,179]
$[CoCp_2]^+$	$[Pd(S_2C_2Ph_2)_2]^-$	–	1:1	**222**	[180]
$[CrCp_2^*]^+$	$[Ni(edt)_2]^-$	CH_3CN	1:1:2	**223**	[179]
$[FeCp_2^*]^+$	$[Ni(bdt)_2]^-$	–	1:1	**224**	[179]
$[MnCp_2^*]^+$	$[Ni(bdt)_2]^-$	–	1:1	**225**	[179]
$[CrCp_2^*]^+$	$[Ni(bdt)_2]^-$	–	1:1	**226**	[179]
$[FeCp_2^*]^+$	$[Ni(tcdt)_2]^-$	–	1:1	**227**	[179]
$[MnCp_2^*]^+$	$[Ni(tcdt)_2]^-$	–	1:1	**228**	[179]
$[CrCp_2^*]^+$	$[Ni(tcdt)_2]^-$	–	1:1	**229**	[179]
$[Fe(cp^*)_2]^+$	$[Ni(bds)_2]^-$	CH_3CN	1:1:1	**230**	[181]
$[Fe(cp^*)_2]^+$	$[Ni(dmit)_2]^-$	–	1:1	**231**	[181]
$[Fe(cp^*)_2]^+$	$[Pd(dmit)_2]^-$	–	1:1	**232**	[182]
$[Fe(cp^*)_2]^+$	$[Pt(dmit)_2]^-$	–	1:1	**233**	[182]
$[Fe(cp^*)_2]^+$	$[Ni(dmid)_2]^-$	CH_3CN	1:1:1	**234**	[183]
$[Fe(cp^*)_2]^+$	$[Ni(dmid)_2]^-$	–	1:1	**235**	[182]
$[Fe(cp^*)_2]^+$	$[Pd(dmid)_2]^-$	–	1:1	**236**	[182]
$[Fe(cp^*)_2]^+$	$[Pt(dmid)_2]^-$	–	1:1	**237**	[182]
$[Fe(cp^*)_2]^+$	$[Fe(dmit)_2]^-$	–	1:1	**238**	[184]
$[Fe(cp^*)_2]^+$	$[Au(dmit)_2]^-$	–	1:1	**239**	[185]
$[Fe(cp^*)_2]^+$	$[Au(dmit)_2]^-$	–	1:3	**240**	[185]
$[Fe(cp)_2]^+$	$[Au(dmit)_2]^-$	–	1:3	**241**	[185]
$[Fe(cp)_2]^+$	$[Au(dmit)_2]^-$	–	1:4	**242**	[186]
$[Co(cp)_2]^+$	$[Ni(dmit)_2]^-$	–	1:1	**243**	[187]
$[Co(cp)_2]^+$	$[Ni(dmit)_2]^{0.33-}$	CH_3CN	1:3:2	**244**	[188]
$[Ni(cp)_2^*]^+$	$[Ni(dmit)_2]^-$	–	1:1	**245**	[189]
$[Mn(cp)_2^*]^+$	$[Fe(dmit)_2]^-$	–	1:1	**246**	[189]
$[Mn(cp)_2^*]^+$	$[Ni(dmit)_2]^-$	–	1:1	**247**	[189]

9.1. Salts with $[M(mnt)_2]^{X-}$ anions

$[M(mnt)_2]^{X-}$ complexes have been widely used as counterions for various substituted ferrocene compounds **187**–**215** and have resulted in a huge variety of different packing motifs. This structural diversity is illustrated by polymorphism in **188α** and **188β** and gives an initial impression that structural systematics may be difficult to elucidate from these salts. The α form has DAADAA (D = metallocene electron donor, A = metal-bis-1,2-dithiolene electron acceptor) chains plus D_2A moieties arranged orthogonal to this forming edge-to-edge chains and contrasts with DADA chains plus isolated DAAD dimers of the β form. In both forms, however, as in the chains of centrosymmetric DAAD units in **187** (Fig. 32), the AA components in the chain are effectively diamagnetic due to strong antiferromagnetic coupling through eclipsed M-over-M interaction and all these salts obeys the Curie–Weiss expression with $\theta = +6.6$ K (**188α**), $+9.8$ K (**188β**) and 0 K (**187**). **188β** exhibits field dependent susceptibility below 7 K consistent with ferromagnetic coupling within the DADA chains.

Dimerisation of the $[M(mnt)_2]^-$ component is a feature repeated in **189**–**192**, however, in other respects these exhibit a range of different packing motifs. The α phase of the $[Co(mnt)_2]^-$ salt **189** and the $[Fe(mnt)_2]^-$ **190** salt are isostructural and are composed of metallocene and dithiolene dimers. Within the $\{[M(mnt)_2]_2\}^{2-}$ units, a square–pyramidal geometry is adopted with an M-over-S arrangement in contrast to the M-over-M arrangement above. The decamethylferrocenium cations form an unusual packing mode with the complexes arranged in a perpendicular manner. Due to the diamagnetic units present in both **189** ($[Co(mnt)_2]^-$ is diamagnetic) and **190** (dimerised dithiolenes), the magnetic metallocene components are unable to form an interacting lattice.

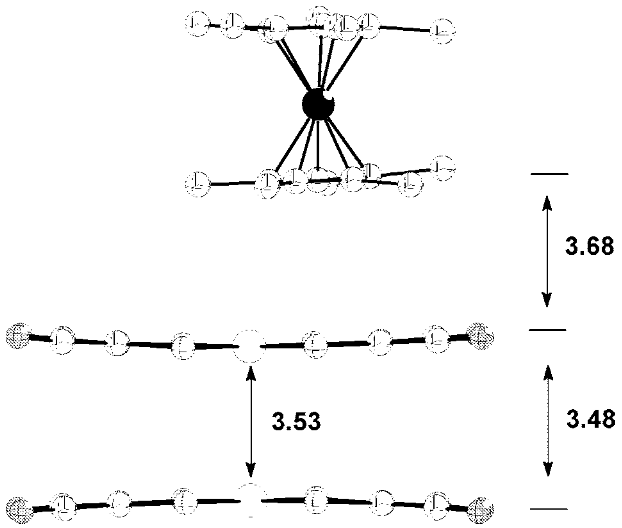


Fig. 32. A representation of the crystal structure of **187**. The nickel atom is represented by the open sphere, the iron atom by the black sphere, the sulphur atoms by the cross-hatched spheres and the carbon atoms by the octants and the nitrogen atoms by the criss-crossed spheres.

The $[Co(mnt)_2]^-$ anion also gives rise to a β phase **191** with a completely different crystal structure which is solvent free. The complexes are arranged in a mixed stack of dianions and dications with the pattern AADD. Again the presence of diamagnetic dianions contributes to the magnetic isolation of the $[Fe(cp^*)_2]^+$ cations. The use of the paramagnetic dianion, however, results in different behaviour. The structure of the $[Cu(mnt)_2]^{2-}$ containing salt **192** shows mixed stacks with the arrangement $A^{2-}D^+D^+A^{2-}D^+D^+$. The magnetic susceptibility was modelled considering DAD triad units characterised by a DA coupling constant $J = -4.8\ \text{cm}^{-1}$ and intertriad interactions modelled by $\theta = 0.27$ K.

In contrast to the $[FeCp_2^*]^+$ salts above, the salt **193**, containing simple $[FeCp_2]$ units shows an unusual 3:2 ratio of metallocene to dithiolene complex. Consideration of the X-ray structure, in particular the Fe–C distances, led to the assignment of the salt as containing two metallocene cations and one neutral ferrocene. The dithiolene complexes form dimers with ferrocenium cations at either end and the neutral ferrocene lies adjacent. No magnetic data were reported.

A series of $[M(mnt)_2]^-$ (M = Ni, Pt) salts with modified metallocene counterions has been isolated (Fig. 33). In an initial study, a crystal structure was obtained for **194** and indicated segregated stacks of anions and cations which contrasts with the mixed stacking observed in the other metallocene-$[M(mnt)_2]^{X-}$ salts discussed above. Within the dithiolene stacks there are long (3.99 Å) and short (3.67 Å)

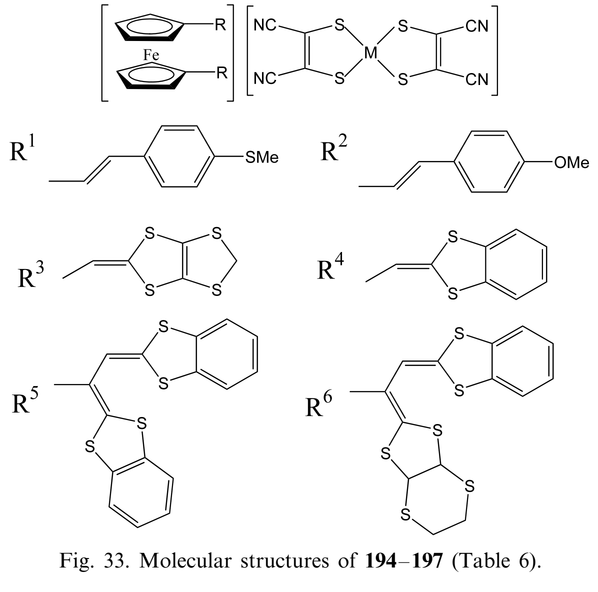


Fig. 33. Molecular structures of **194**–**197** (Table 6).

Ni···Ni distances, indicating some dimerisation with the intradimer units in an ca. eclipsed formation. Magnetic susceptibility measurements of salts **194–197** were carried out and for **194–196** show a component arising from $\{[\mathrm{Ni(mnt)_2}]^-\}_2$ dimers with a singlet ground state and thermally accessible triplet state. The salt **197** showed a possible phase change but lack of structural data prevented further analysis.

Subsequent studies led to the preparation of the salts **198–203** and **204–212** using related ferrocene moieties with, for example, alkylthio substituents. The X-ray structures of **198** and **200–203** were determined and the Ni containing salt **198** and the corresponding Co containing salt **200** contain similar structural motifs consisting of stacks of $[\mathrm{M(mnt)_2}]^-$ anions surrounded by columns consisting of pairs of ferrocenium cations. Within the dithiolene stacks, dimerisation occurs to give alternating Ni···Ni distances, and in the case of **200**, strong centosymmetric dimers. These salts and the related **199** showed Curie–Weiss behaviour with Θ values small and negative or zero. The salts **201** and **202** are isomorphous and consist of alternating layers of ferrocenium cations and dithiolene anions, thus a DADA structural motif is formed running along two different crystal directions (Fig. 34). The magnetic behaviour of these shows a positive value of Θ of about 3 K indicating some ferromagnetic coupling which may be associated with the alternating donor–acceptor nature of the salts. In contrast, **203** shows dimerisation of the $[\mathrm{Co(mnt)_2}]^-$ units and a structure best described as $\mathrm{DA_2D}$ type repeat unit. This leads to essentially isolated ferrocenium species and Curie–Weiss magnetic behaviour with $\Theta = 0$.

Salt **204** shows isolated $\{[\mathrm{Ni(mnt)_2}]^-\}_2$ dimers with ferromagnetic interaction contrastingly greatly with the analogous salt **201** with more Me groups on the ferrocene units. The dimers show a unique, non-planar Ni over C=C arrangement and are the first example of an antiferromagnetic, isolated $\{[\mathrm{Ni(mnt)_2}]^-\}_2$ dimer. The $[\mathrm{Pt(mnt)_2}]^-$ salt with the same ferrocene unit (**205**) shows a DADA alternating chain with every cation surrounded by six anions in a 3-D arrangement. Similar to **201** and **202**, this led to ferromagnetic ordering at low T as indicated by a strong increase in χT below 20 K and a Weiss constant of $+3$ K. In salts **206** and **208**, antiferromagnetic dimmers of the dithiolene complexes were observed and although the crystal structure for **207** was not obtained, the magnetic data were consistent with a similar structure. Salt **210** shows a segregated stack structure with solvent molecules intercalated into the anion stacks. The magnetic behaviour is complex, probably due to multiple intermolecular contacts between the components, but indicates strong antiferromagnetic interactions. Full

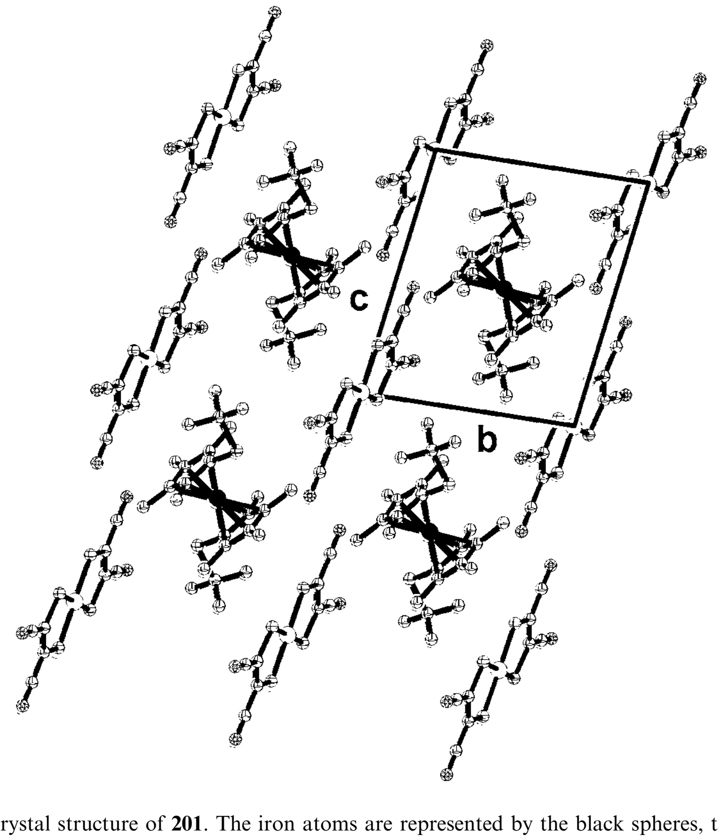


Fig. 34. A representation of the crystal structure of **201**. The iron atoms are represented by the black spheres, the nickel atoms as empty spheres, the sulphur atoms by the cross-hatched spheres, the carbon atoms by the octants, and the nitrogen atoms by criss-crossed spheres.

study of the properties of **209**, **211** and **212** was limited by the lack of structural data.

9.2. Salts with other dithiolenes

The great structural diversity which can be achieved by changes to the component complexes is illustrated by replacement of $[Ni(mnt)_2]^-$ with $[Ni(tfd)_2]^-$ to give **216**. In contrast to **187**, this consists of centrosymmetric DADA chains and the dimerisation characteristic of mnt complexes is absent. Magnetic behaviour is, therefore, not dominated by strong antiferromagnetic coupling of the dithiolene component and magnetic susceptibility ca. follows the Curie–Weiss law with estimates of θ as $+5$ to $+15$ K. The effective moment rises with decreasing temperature to 4.2 K and a marked field dependence below 8 K of the susceptibility was observed suggesting the interaction along the chains is ferromagnetic. No bulk 3-D ordering was observed, however, down to 2.15 K, the lowest temperature obtained.

A further series of salts has been prepared using the $[M(tfd)_2]^-$ complexes and containing the $S=1$ metallocene $[MnCp^*_2]^+$. Of these, only **217** was characterised by X-ray crystallography and consists of an alternating DADA stack isostructural with the analogous salt **216**. The salts **218** and **219** were shown by powder X-ray data to be isostructural with **217**. All three salts were found to behave as metamagnets with a field induced transition from an antiferromagnetic to a ferromagnetic state. This was illustrated through a study of the field dependence of the magnetisation against temperature curves, which showed stabilisation of a ferromagnetic ground state as the field is increased above 2500–3000 G. These data were interpreted as indicating a strong ferromagnetic intrachain coupling and a weak antiferromagnetic interchain coupling. This differs from the related salt **216** by the increased spin on the metallocene leading to a stronger intrachain interaction. Salts **220**, **221** and **222** also use dithiolenes different in structure from the majority studied. In the case of **222**, this leads to alternating DADA chains and again this may be linked to the non-planar nature of the dithiolene complex that discourages dimerisation of the anionic units.

A series of salts has been prepared using $[Ni(bdt)_2]^-$, $[Ni(edt)_2]^-$ and $[Ni(tcdt)_2]^-$ anions **220**, **221** and **223**–**229** and has resulted in some interesting magnetic behaviour. X-ray structures for **220** and **221** were isostructural and showed an alternating DADA stack arrangement. This also represents the first reported structures of $[Ni(edt)_2]^-$. In contrast, salts **224**, **226** showed stacks with a DDADDA arrangement separated by acceptor layers, similar to the structure of **230**. Although all these salts showed Curie–Weiss behaviour at $T > 50$ K, with a negative Weiss constant, behaviour at lower temperatures was more varied. In particular, **224**, **225** and **226** showed an increase in χT around 3–5 K consistent with ferromagnetic interactions and metamagnetic behaviour was demonstrated for **221** and **225**. These features were explained in terms of dominant ferromagnetic interactions within the DADA chains with antiferromagnetic interactions between the chains. This is similar to the behaviour shown by **217**–**219**.

A number of mixed metallocene-dithiolene salts have been prepared based on the $[Ni(dmit)_2]^-$ anion and O or Se containing analogues, well known to be able to form partially oxidised conducting and superconducting crystals in addition to the possibility of magnetic interactions. Thus, a series of related salts was studied of general formula $[Fe(Cp^*)_2][M(dmix)_2]$ **231**–**237** including structural characterisation for **231**, **233**, **234**, **236** and **237**. Generally, these were found to follow the Curie–Weiss law above 100 K. Salt **232** showed a positive Weiss constant of $+2.6$ K. This was interpreted in terms of predominantly ferromagnetic interactions, however, no magnetic ordering was observed down to 2 K. Similar behaviour was observed for **234**. Salt **231**, consists of DDAA chains in which side-by-side pairs of metallocene cations alternate with face-to-face pairs of dithiolene anions. Magnetic susceptibility measurements indicated ferromagnetic interactions as evidenced by an increase in $\chi_M T$ below 25 K reaching a maximum at 2.1 K. This is attributed to interactions within the DDAA units. The rapid reduction of $\chi_M T$ below 2.1 K is interpreted as antiferromagnetic interactions between these units. In the same study, the related salt containing $[Ni(bds)_2]^-$ **230**, showed a more complex structural motif comprising layers of DDA stacks which also have side-by-side metallocene units. These are separated by sheets of $[Ni(bds)_2]^-$ anions. Magnetic susceptibility measurements of **230** show that $\chi_M T$ continues to increase until the lowest attainable temperature of 1.5 K, indicating dominant ferromagnetic interactions within this temperature range, although no spontaneous magnetisation or hysteresis could be observed at 1.9 K.

The salt $[Fe(cp^*)_2][Fe(dmit)_2]$ **238** consists of two crystallographically independent centrosymmetric dimers of the dithiolene units with an Fe over S arrangement leading to a square–pyramidal geometry around Fe. This is reminiscent of the tetrabutyl ammonium salt of $[Fe(dmit)_2]^-$ as well as the complexes $[NBu_4][Fe(mnt)_2]$ [8] and $[NBu_4][Fe(tdas)_2]$ [120] and the result is strong antiferromagnetic interaction between the Fe centres. Two independent cations are also present.

Further examples of partially oxidised salts were prepared by electrochemical oxidation of $[NBu_4][Au(dmit)_2]$ in the presence of $[Fe(cp^*)_2]$ and $[Fe(cp)_2]$ to afford **240** and **241**. These behave as semiconductors with r.t. conductivity of 0.093 and 0.12 S

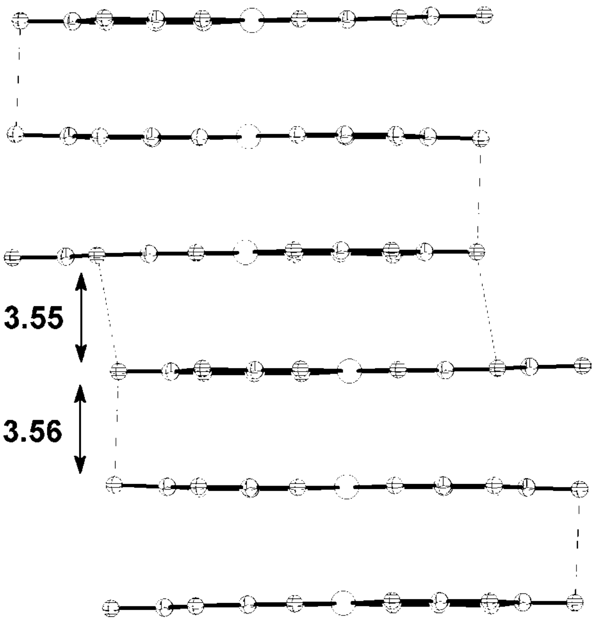


Fig. 35. A representation of the crystal structure of **244**. The nickel atoms are represented by the open spheres, the sulphur atoms by the cross-hatched spheres, and the carbon atoms by the octants. The metallocene counter ions have been omitted for clarity to show the triads of the $[Ni(dmit)_2]$ units. The S···S interactions are shown by the dotted lines.

cm^{-1}, respectively. This can be compared with other partially oxidised salts $[Fe(cp)_2]_{0.25}[Au(dmit)_2]$ (**242**) and $[Fe(cp)_2]_{0.2}[Au(C_3Se_5)_2]$ prepared by mixing of $[Fe(cp)_2]^+$ with the appropriate dithiolene monoanion. These salts show similar conductivities of 0.10 and 0.16 S cm^{-1}, respectively. The lack of structural data, however, makes further interpretation difficult. An X-ray structure of the related salt **239** shows a 1-D chain of dimerised diamagnetic Au complexes with the cations located between the anion arrays.

Only one example of a structurally characterised, partially oxidised metal dithiolene complex with metallocene counterion has been reported **244**. Preparation and crystallisation was achieved via electrochemical oxidation of $[NBu_4][Ni(dmit)_2]$ in the presence of $[Co(Cp)_2]PF_6$. This salt showed semiconductive behaviour with r.t. conductivity of 0.06 S cm^{-1}. The structure is composed of stacked centrosymmetric triads with interplanar distances within and between triads almost identical at 3.56 and 3.55 Å, respectively, but with a transverse shift of complexes along the long molecular axis between triads (Fig. 35). These stacks are formed into 2-D sheets separated by the cobaltacenium counterions. The cobaltacenium units are shown to be diamagnetic monocations bearing a full positive charge by consideration of the C–C bond length.

Salts **245**, **246** and **247** involve paramagnetic $[M(cp^*)_2]^+$ cations with M = Ni and Mn. Although structural data has not been obtained for these, **247** shows interesting long-range ferromagnetic order with T_c around 2.5 K.

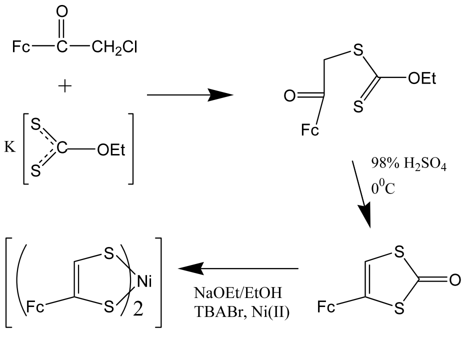
In conclusion, an initial survey of this class of materials suggests enormous structural diversity with little indication of guiding principles for future material preparation. Closer inspection, however, reveals that many aspects of these salts are familiar to other types of metal-1,2-dithiolene structures. This is illustrated by the tendency of $[M(mnt)_2]^-$ complexes to dimerise in the presence of relatively large counterions. The resulting influence of these large diamagnetic components is generally to magnetically isolate the paramagnetic metallocene components and reduce the possibility of unusual features in the magnetism of the salt. $[M(dmit)_2]^{X-}$ salts, however, have led to some examples of non-integral oxidation state materials in keeping with the superior ability of these complexes to achieve such materials with other counterions. The relatively large metallocene counterions, however, seem to encourage semiconductor formation in analogy with $[Ni(dmit)_2]^-$ salts with other families of cation. It may be that large counterions are unsuitable for the formation of metallic salts as they encourage a non-uniform stack of the dithiolene complexes leading to electron localisation.

The combination of metallocene and dithiolene complexes into mixed salts has shown promise for the preparation of materials that show ferromagnetic interactions. In particular, the preparation of mixed stacks with alternating donor and acceptor moieties is seen to be favourable for such interactions. This is in keeping with related metallocene-containing materials with other electron acceptor counterions where ferromagnetic interactions in mixed stacks is interpreted in terms of the McConnell spin polarisation model [168]. There is some indication, that the choice of dithiolene to minimise the likelihood of dimerisation can increase the possibility of mixed-stack formation, e.g. using $[Ni(tfd)_2]^-$. Of course, achievement of 3-D ferromagnetic ordering depends on all intermolecular interactions and not just those within stacks and difficulties arise with the lack of any real method of controlling the interstack structure to maximise the chance of achieving a particular packing motif. Clearly, the range of different packing arrangements displayed among many salts described shows little apparent pattern to guide future studies. An exception to this may be the salts **198**–**203** and **205** where introduction of the larger ^{t}Bu group in place of Me appears to inhibit adjacent packing of metallocenes and, therefore, promote an alternation of donor and acceptors. Further work will illustrate whether this can be developed into a consistent strategy.

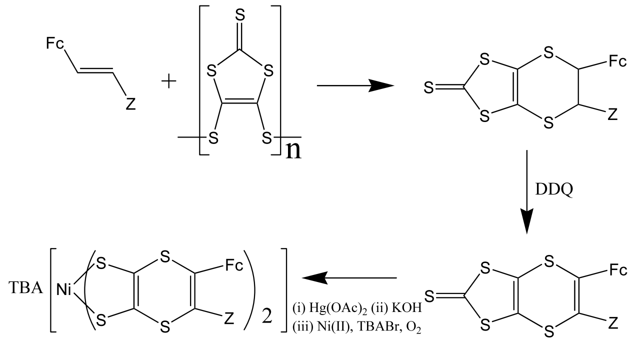
In contrast with their simpler salts, $[M(tfd)_2]^-$ salts with metallocene counterions have led to some of the most magnetically interesting salts in this section. It may be that the poor ability of these dithiolene complexes to form close intermolecular interactions has proven beneficial in this area in reducing the tendency towards diamagnetic dimers and has promoted the formation of mixed DADA stacking. This may indicate that many of the complexes, such as those in Section 2, which have not shown great utility in conducting materials, due to bulky end groups preventing close stacking, may paradoxically be likely to produce mixed-stack salts with metallocenes and maximise the chances of preparing ferromagnetic materials.

9.3. Covalently attached metallocenes

Several complexes have been prepared which involve covalent attachment of ferrocene units to metal dithiolene centers. In addition to the possibility of preparing hybrid magnetic | conducting materials, this has been motivated by the opportunity to prepare multi-centre redox species and extended conjugated molecules. The reaction of a ferrocenealdehyde with xanthate ester followed by a cyclisation procedure (Scheme 4) gave a ketone precursor, which could be deprotected and used to form dithiolene complexes [190]. This procedure represents an important general route to many dithiolene systems. The resulting Ni complex **248**, shows a 20° twist of the ferrocene group out of the plane of the dithiolene core, however, this may be influenced by packing considerations. Electrochemical study showed three sequential oxidations. An analogous species with four ferrocene substituents was reported and studied primarily for its optical properties [191]. A complex containing four SCH_2Fc (Fc = ferrocene) groups attached to a central Ni-bis-1,2-dithiolene ($Ni(S_2C_2)_2$) core **249** was prepared [192], however, the saturated link between the metal centres limits the possibility of communication between the ferrocene and dithiolene units as evidenced by electrochemical study. Reaction of the polymer $(C_3S_5)_n$ with ethylene groups can lead in general to suitable precursors for dithiolene complexes and this approach has been exploited in the preparation of **250** (Z = Fc) and **251** (Z = H) (Scheme 5) [193,194]. Again the structures of these show ferrocene units twisted out of the plane of the dithiolene unit.



Scheme 4. Preparation of the ferrocene-containing complex **248**.



Scheme 5. Preparation of the ferrocene-containing complexes **250** (Z = Fc) and **251** (Z = H).

This approach remains an attractive and promising route to novel molecules and materials. To achieve unexpected new properties the conjugated link between the dithiolene and metallocene components must be maximised such that extended delocalised species can be prepared reminiscent of the TTF-containing dithiolenes in Section 6, which have led to exciting new conductivity properties.

10. Conclusions

The primary goal of this work is to highlight the enormous variety of metal-bis-1,2-dithiolene complexes which have been used in the construction of crystalline conducting or magnetic assemblies or have the potential to be used in this way. Despite the large variety of complexes now available, much work still focuses around familiar complexes such as $[M(dmit)_2]^{X-}$ and $[M(mnt)_2]^{X-}$ and indeed these continue to lead to new and unusual materials. The continued exploration of new complex families, however, has opened up completely novel materials and properties, and has the potential to overcome problems and limitations associated with well-established examples. This has been facilitated by the establishment and exploitation of several straightforward routes to new dithiolene complexes, offering the possibility to design and prepare new complexes of choice. In this context, dithiolenes extended with TTF units have shown properties unique among these or any other materials and have led to a single-component metallic conductor. In the field of molecular magnetism, typical behaviour patterns for several salts have begun to emerge and, based on this, new complexes that show a reduced tendency to form diamagnetic dimers offer opportunities in the preparation of materials with improved properties compared with those currently known. This has led in the previous decade to materials containing metal-bis-1,2-dithiolenes that are ferromagnets, metamagnets, spin ladders and hybrid conducting | magnetic systems. In addition, such studies have led to progress in other areas of application that also utilise these complexes such as NLO materials and laser dyes. Future work must take the opportunity to build on the current understanding of the way these molecules assemble. Thus new studies must be increasingly target driven, and involve preparation of particular material types by rational analysis of the known behaviour of the component building blocks or by synthesis of new building blocks expected to possess, not only the required molecular properties, but also the likelihood that they will interact in a predetermined way in the solid state.

It is hoped that this summary will give more insight into the diverse range of experimentally accessible materials and allow a coalescence of knowledge between individual areas. Our structural and physical understanding of these materials coupled with knowledge of the properties they possess should provide a route to the modelling, design and synthesis of materials with pre-designed properties.

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