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Review

Coordination polymers of sulphur-donor ligands



Emily J. Mensforth^{a,b}, Matthew R. Hill^b, Stuart R. Batten^{a,*}

^aSchool of Chemistry, Monash University, Clayton, Vic. 3800, Australia

^bCSIRO Materials Science and Engineering, Private Bag 33, Clayton South MDC, Vic. 3169, Australia

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ABSTRACT

This review gives an account of the coordination polymers that can be attained with ligands containing the sulphur-based dithiocarbamate (dtc), dithiocarboxylate and xanthate functional groups. The coordination modes adopted by the different sulphur-based ligands are discussed, and methods of attaining higher dimension complexes outlined. The review also addresses potential applications of such materials.

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Emily Mensforth Ms Emily Mensforth completed her Bachelor of Applied Chemistry (Honours) from RMIT University in 2007 and is currently pursuing a PhD in the area of Coordination Polymers at Monash University in collaboration with CSIRO.



Matthew Hill Matthew Hill obtained his PhD in 2006 in inorganic materials chemistry from the University of New South Wales. Matthew then joined the CSIRO to work in the area of porous materials. He leads research into energy and gas storage and also has interests in separations, with a particular focus on metal organic frameworks. Target applications include carbon dioxide capture, natural gas purifications, and gaseous fuels storage. The CSIRO materials hold numerous records for performance. The team also recently showed these MOFs can filter substances from water, including toxic pesticides. Matthew is the 2011 Victorian Young Tall Poppy of the Year and 2012 Eureka Prize winner for Emerging Leadership in Science.

* Corresponding author. Tel.: +61 399054606; fax: +61 399054597.

E-mail address: stuart.batten@monash.edu (S.R. Batten).



Stuart Batten Stuart Batten completed his PhD (1996) at the University of Melbourne with Richard Robson and Bernard Hoskins. This was followed by postdoctoral positions at Bristol, Melbourne and Monash, including two Australian Research Council Fellowships. He commenced a Lectureship at Monash in 2006, and was promoted to Senior Lecturer in 2007, Associate Professor in 2009, and currently holds a Future Fellowship. His research, detailed in more than 250 publications, is mainly in the areas of crystal engineering, coordination polymers, supramolecular chemistry, inorganic chemistry, and crystallography. He is also lead author of a book entitled *Coordination Polymers: Design, Analysis and Application* (RSC 2009; with DR Turner and SM Neville). His research has attracted over 15,000 citations (h-index = 62) and been recognised by a Thomson Scientific Citation Award (2008), the Le Févre Memorial Prize (2008), the Rennie Memorial Medal (2002), and several other awards.

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1. Introduction

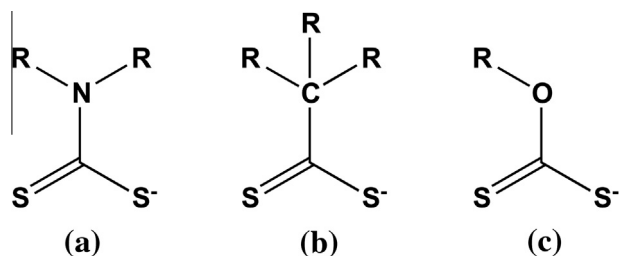
The synthesis of coordination polymers (CPs) is a rapidly growing field in chemistry as well as materials science. CPs can be tailored to display various chemical and/or physical properties, resulting in promising materials in terms of magnetism, conductivity, nonlinear optical responses, catalysis, gas storage and ion exchange [1]. Judicious choice of the ligand(s) used to construct a CP is vital, with ligands typically bearing two divergent coordination sites (or in some instances higher connectivity). Commonly these coordination sites contain N or O donors, for example pyridyl, imidazole, nitrile or carboxylate functional groups [1]. These ligands are then combined with a range of metal centres that are capable of adopting various coordination geometries, resulting in a large and ever expanding range of CP materials.

Despite this growing range of CP complexes, there are still many more CPs yet to be synthesised and explored; in particular ligands with sulphur coordination sites have received far less attention. CPs with N and O donor ligands have shown promising results in regards to gas adsorption and catalysis, and materials demonstrating impressive conductive, electronic and magnetic properties have also been reported. However, it is expected that sulphur-rich ligands with expanded highest occupied molecular orbitals

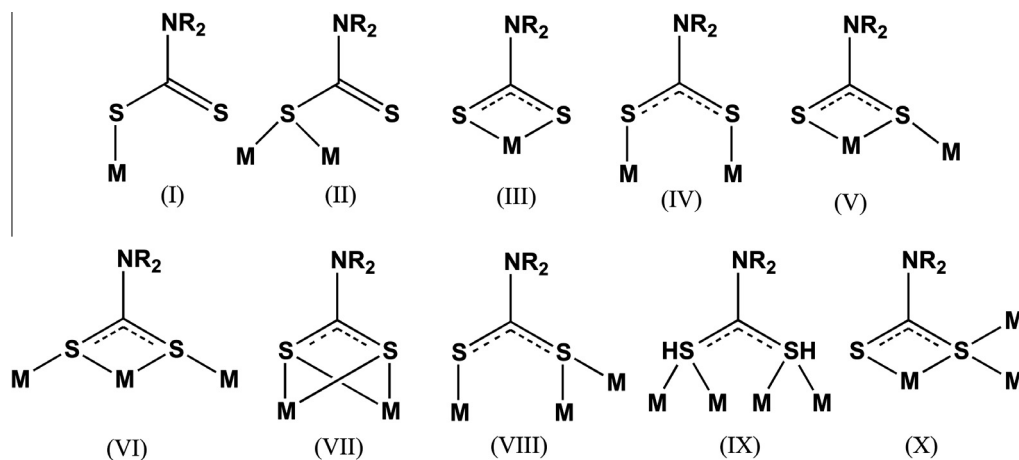
(HOMOs) will allow for strong metal–metal interactions, whereby improved electro-conductive materials can be generated. Sulphur-based ligands, such as the 1,1-dithiolate family, have proved promising when reacted with transition metals to give rise to a variety of metal clusters possessing interesting conductive properties. These ligands, however, are yet to be explored in as much depth when it comes to CPs, particularly in comparison to the related carboxylate type ligands [2].

The 1,1-dithiolate family consists of a variety of sulphur-containing ligands such as dithiocarbamates, dithiocarboxylates, phosphor-1,1-dithiolates, dithioarsinates, and xanthates, and the versatility of a wide range of coordination motifs allows for flexible metal complexes that are capable of imparting interesting properties and have applications in materials and separation science [3]. For the purpose of this review we focus on three of these ligands; the dithiocarbamate (dtc), dithiocarboxylate and xanthate as shown in *Scheme 1*.

A great deal of attention has been given to metal clusters of these sulphur-based ligands, due to the ability of the two sulphur atoms to chelate metal centres. In addition to these strong coordinative bonds, the resonance between the two sulphur atoms gives rise to a variety of coordination patterns (detailed in greater depth below), which allows for a number of metal oxidation states to be stabilised. The ligands depicted in *Scheme 1* commonly chelate to form four-membered rings with transition metals, and as such these materials have been extensively investigated and thoroughly reviewed [3–7]. These reviews focussed mainly on the chemical redox behaviour of the 1,1-dithio ligands, particularly dtc and xanthates. They also describe the synthetic difficulties in obtaining these ligands as acids; instead the ligands are generated *in situ* or alkaline metal precursors are prepared, in order to counteract the instability of the protonated acid compounds. In addition to these synthetic challenges, the literature is lacking in polymeric 1,1-dithiolate-containing complexes, which is due to their strong metal-to-ligand interactions, making it difficult to crystallise polymeric complexes that can be structurally characterised. Recent advancements in technology, such as synchrotron radiation, have



Scheme 1. 1,1 Dithiolate ligands to be reviewed herein: (a) dithiocarbamate (dtc), (b) dithiocarboxylate and (c) xanthate. (Where R = alkyl).



Scheme 2. Various bonding modes of dtc based ligands.

meant that some of these hurdles can be overcome, and thus there have still been a small number of polymeric metal complexes containing dtc, dithiocarboxylate and xanthate ligands reported in the literature. These studies are far outnumbered by metal cluster compounds with the same ligands, however it is a growing area with great promise.

Herein we review polymeric compounds containing ligands with the 1,1-dithiolate functionalities dithiocarbamate (dtc), dithiocarboxylate and xanthate. The different bridging and coordination modes observed in the formation of polymeric complexes will be detailed and applications for specific complexes explored.

2. Dithiocarbamates

The dithiocarbamate (dtc) functional group is usually obtained via a CS₂ insertion reaction with a primary or secondary amine. As with its 1,1-dithiolate parent family, the dtc functional group is a versatile coordinating group due to the large ionic radii of the sulphur atoms. The resonance between the two sulphur atoms also allows for various coordination modes to be adopted, as detailed in Scheme 2. Such properties give rise to dtc-based complexes that are useful for applications in medicine [8], agriculture [9], organic syntheses [10], and more recently metal deposition and metal sulphide nanoparticles [11–13]. Much attention over the past century has focussed on metal dtc clusters, and as such a number of reviews detailing these dtc cluster materials have already been published [3,5,6]. Herein we focus primarily on polymeric coordination complexes containing dtc ligands and the structural motifs observed in such complexes.

The most common binding mode of dtc is mode III (Scheme 2), however this mode along with modes I, II and IV will only lead to mononuclear or dinuclear clusters if a single dtc-based ligand with only one dtc functionality is involved. Incorporation of modes V–X, or a combination of these, has been observed in numerous polymeric complexes (Table 1), however overall analysis of dtc metal complexes in the Cambridge Structural Database (CSD, version 5.33 of May 2012) [14] reveals polymeric species to be rare (<4%), despite this ability of the dtc ligand to adopt various coordination modes and capture a number of metal complex geometries. A survey of crystallographically characterised polymeric dtc networks showed that more than 80% were 1D chains, while 2D sheets only accounted for less than 10%, and 12% were 3D in nature. The formation of these dtc containing extended networks can occur through a variety of methods: bridging and chelating dtc groups, bridging anions (such as halides, nitrate or cyanide), or bridging co-ligands. The key to forming dtc metal net-

works of 3D nature is the presence of di-topic groups within the ligand of choice.

2.1. Polymerisation through clustering of metal centres

Numerous 1D polymeric chains have been isolated through the exploitation of the dtc ligand's versatile bonding (see Scheme 2). These complexes have been discovered by a number of different research groups and the research focus varies from conductive materials [24,25,27] to magnetic materials [19]. The majority of these 1D chains have been obtained with second and third row transition metals, such as Ag [30,31,33], Pb [50], Cd [34], Au [46] and Hg [47,49], with only two dtc coordination complexes obtained with the first row transition metals Mn [19] and Cu [21].

The orientation and overall packing of the 1D chains are largely influenced by the metal's ionic radius and/or charge. This has been observed with Ag [30] and Mn [19], as different 1D chains were isolated with the same diethyl-dtc ligand. Similar structural differences have also been observed with this ligand and Cu [21] and Cd [34]. In addition the size of the organic group influences the overall packing, with the chain formation being effected by steric hindrance or packing interactions between the chains. When the simple diethyl-dtc ligand is reacted with Ag, a 1D ribbon structure along the *c* axis (Fig. 1a) is formed by trigonally and tetrahedrally coordinated metal centres being μ_3 -bridged by κ^3 - and κ^4 -S₂CNC₂H₅ ligands [31]. Reaction between Ag and the bulkier dibenzyl-dtc gives rise to helical 1D chain [33], which has each metal centre coordinating to four sulphur atoms from two dtc ligands (ie. κ^4 -S₂CN(CH₂C₆H₅)₂). The packing of these helical chains is also further influenced by edge-to-face π - π interactions between the chains as shown in Fig. 1b.

2.2. Inclusion of bridging anions

Another method of producing 1D chains involves the bridging of metal centres with included counterions such as halides, cyanide or nitrate. The ability of these anions to both charge balance and bridge is particularly relevant for forming polymeric structures when large metal clusters are involved. When the only bridging method is the inclusion of counterions, and all dtc ligands are coordinating through the standard chelating η^2 (S,S') mode III (Scheme 2), then simple 1D chains can be observed. However, this has only been reported for the post transition metal Bi [51–53,55] and the metalloid Sb [43]. Alternatively, when the extended binding capabilities of the dtc functional group and the bridging capabilities of halides are combined, numerous materials have been produced,

Table 1
Dithiocarbamate (dtc) complexes.

Complex	S-ligand	Coordination mode	Dimensionality	Refs.
[Na(S ₂ CN(CH ₂ CH ₂ OH)CH ₂ CH ₂ CH ₃)]	(2-hydroxyethyl)(propyl)-dtc	I	2D	[15] ^a
[K(S ₂ CN(CH ₂ CH ₂ OH) ₂)]	bis-(2-hydroxyethyl)-dtc	VII	3D	[15] ^a
[K ₂ {(S ₂ CN(CH ₃)CH ₂) ₂ }]·(CH ₃ CH ₂ OH) ₂	ethane-1,2-diylbis(methyl)-dtc	VII	2D	[16]
[K ₂ {(S ₂ CN(CH(CH ₃))CH ₂) ₂ }]·(CH ₃ CH ₂ OH) ₂	ethane-1,2-diylbis(isopropyl)-dtc	X	2D	[16]
[K ₂ (C ₁₈ H ₁₈ N ₂ S ₄)(H ₂ O) ₄]	<i>N,N'</i> -dibenzyl-1,2-ethylenebis-dtc	II	2D	[17]
[Rb ₂ (C ₁₈ H ₁₈ N ₂ S ₄)(H ₂ O)]	<i>N,N'</i> -dibenzyl-1,2-ethylenebis-dtc	VII	3D	[17]
[Cs ₂ (C ₁₈ H ₁₈ N ₂ S ₄)(H ₂ O)]	<i>N,N'</i> -dibenzyl-1,2-ethylenebis-dtc	VII	3D	[17]
[Cs(S ₂ CN(CH ₂ CH ₂ OH) ₂)]	bis-(2-hydroxyethyl)-dtc	VII	3D	[15] ^a
[Cr(S ₂ CN(CH ₂ CH ₃) ₂) ₃]·2CuI	diethyl-dtc	V and VI	1D	[18] ^b
[Cr(S ₂ CNC ₅ H ₁₀) ₃]·3CuI	pyrrolidine-dtc	V and VI	1D	[18] ^b
[Mn ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	V	1D	[19]
[Co(S ₂ CNC ₄ H ₈) ₃]·3CuBr	pyrrolidine-dtc	V and VI	1D	[20] ^b
2[Co(S ₂ CN(CH ₂ CH ₂ CH ₂ CH ₃) ₂) ₃]·5CuI	dibutyl-dtc	V and VI	1D	[20] ^b
[Cu ₂ (S ₂ CNCH ₃) ₂]	dimethyl-dtc	V	1D	[21]
[Cu ₂ Cl ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	V	1D	[22]
[CuBr] ₂ [Co(S ₂ CN(CH ₂ CH ₃) ₂) ₃]	diethyl-dtc	V and VI	1D	[23] ^b
[Cu ^I ₄ Cu ^{II} (S ₂ CN(CH ₂ CH ₃) ₂) ₂ Cl ₃]	diethyl-dtc	VI	2D	[24] ^c
[Cu ^I ₄ Cu ^{II} Br ₄ (S ₂ CNC ₄ H ₈) ₄]	pyrrolidine-dtc	VI	3D	[25] ^c
[CuI][Co(S ₂ CNC ₄ H ₈) ₃]	pyrrolidine-dtc	VI	1D	[23] ^b
[Cu(S ₂ CNC ₅ H ₁₀) ₂ (CuBr) ₄]	piperidine-dtc	VI	2D	[26] ^c
[Cu(S ₂ CNC ₅ H ₁₀) ₂ (CuBr) ₆]	piperidine-dtc	VI	2D	[26] ^c
[Cu ^I ₂ Cu ^{II} Br ₂ (S ₂ CNC ₆ H ₁₂) ₂ (CH ₃ CN) ₂]	hexamethylene-dtc	V	1D	[27] ^c
[Cu ^I ₂ Cu ^{II} I ₂ (S ₂ CNC ₆ H ₁₂) ₂ (CH ₃ CN) ₂]	hexamethylene-dtc	V	1D	[27] ^c
[Cu ₅ (S ₂ CNC ₅ H ₁₀) ₂ Br ₄]	hexamethylene-dtc	VI	2D	[26] ^c
[Cu ^I ₄ Cu ^{II} I ₄ (S ₂ CNC ₅ H ₁₀) ₂ (CH ₃ CN) ₂]	4-morpholine-dtc	VI	3D	[28] ^c
[Rh(S ₂ CNC ₅ H ₁₀) ₃]·3CuI	pyrrolidine-dtc	VI	1D	[18] ^b
[Pd ₃ (S ₂ CN(CH ₂ CH ₃) ₂) ₆]	diethyl-dtc	V	1D	[29]
[Ag ₆ (S ₂ CN(CH ₂ CH ₃) ₂) ₆]	diethyl-dtc	IV, VIII and IX	1D	[30]
[Ag(S ₂ CN(CH ₂ CH ₃) ₂)]	diethyl-dtc	VI	1D	[31]
[Ag(S ₂ CN(CH ₂ CH ₃) ₂)(P(C ₆ H ₅) ₂ CH ₃)]	diethyl-dtc	V	1D	[32] ^d
[Ag(S ₂ CN(CH ₂ CH ₃) ₂)(P(C ₆ H ₅) ₂ CH ₂ CH ₂ CH ₂)P(C ₆ H ₅) ₂]	diethyl-dtc	III	1D	[32] ^e
[Ag(S ₂ CN(CH ₂ C ₆ H ₅) ₂)]	dibenzyl-dtc	VI	1D	[33]
[Cd(S ₂ CN(CH ₃) ₂) ₂]	diethyl-dtc	V	1D	[34]
[Cd(S ₂ CN(CH ₂ CH ₃) ₂) ₂ (C ₁₂ H ₁₂ N ₂) ₂]	diethyl-dtc	III	1D	[35] ^e
[Cd ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₄ (C ₁₂ H ₁₀ N ₂) ₂]	diethyl-dtc	III	1D	[36] ^e
[Cd(S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	V	1D	[37] ^c
[CH ₃ Cd(S ₂ CN(CH ₃)CH ₂ CH ₂ CH ₂ N(CH ₃) ₂) ₂]	trimethyl-propylenediamine-dtc	III	1D	[38] ^a
[In(CH ₂ CH ₃) ₂ (S ₂ CN(CH ₃)CH ₂ CH ₂ CH ₂ N(CH ₃) ₂) ₂]	(3-isopropylamino)propyl(methyl)-dtc	III	1D	[39] ^a
[CH ₃ Sn(S ₂ CN(CH ₂ C ₆ H ₅)CH ₂ CH ₂ CO ₂) ₂]	<i>N</i> -benzyl-3-aminopropionic-dtc	III	1D	[40] ^a
[(CH ₃ SnCl) ₂ (C ₆ H ₅ CH ₂ N(CS ₂)CH ₂ CH ₂ N(CS ₂)CH ₂ C ₆ H ₅)]	ethane-1,2-diylbis(benzyl)-dtc	III	1D	[41]
[(CH ₃ CH ₂ CH ₂ CH ₂ SnCl) ₂ (C ₆ H ₅ CH ₂ N(CS ₂)CH ₂ CH ₂ N(CS ₂)CH ₂ C ₆ H ₅)]	ethane-1,2-diylbis(benzyl)-dtc	III	1D	[41]
[(CH ₃ SnCl) ₂ (N(CH ₂ CH ₂)N(CH(CH ₃) ₂)CS ₂) ₂]	tris-dtc (see Scheme 3b)	III		[41]
[Sb ₂ I ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	III	1D	[42] ^c
[SbI ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	III	1D	[43] ^c
[Pt ₃ (S ₂ CN(CH ₂ CH ₃) ₂) ₆]	diethyl-dtc	V	1D	[44]
[PtBr ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	VI	1D	[45] ^c
[PtCl ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	VI	1D	[45] ^c
[Au ₂ (S ₂ CN(CH ₂ CH ₂ OCH ₃) ₂) ₂]	bis- <i>N,N'</i> -bis(methoxyethyl)-dtc	IV	1D	[46]
[Hg ₅ (S ₂ CN(CH ₂ CH ₃) ₂) ₈]	diethyl-dtc	IV and V	1D	[47]
[Hg ₂ Br ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	V	1D	[48]
[Hg ₂ (S ₂ CNC ₅ H ₁₀) ₃]	hexamethylene-dtc	IV and V	1D	[49]
[Pb(S ₂ CNC ₅ H ₁₀) ₂]	pyrrolidine-dtc	VII	1D	[50]
[Bi ₂ I ₂ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	III	1D	[51] ^c
[Bi ₂ Cl ₄ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	III	1D	[52] ^c
[Bi ₂ Br ₄ (S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	III	1D	[52] ^c
[Bi ₂ (S ₂ CNCH ₂ CH ₂ CH ₂ CH ₃) ₄ (NO ₃) ₂]	dibutyl-dtc	III	1D	[53] ^f
[BiCl(S ₂ CN(CH ₂ CH ₃) ₂)(C ₆ H ₅)]	diethyl-dtc	III	3D	[54] ^c
[BiI(S ₂ CN(CH ₂ CH ₃) ₂) ₂]	diethyl-dtc	III	1D	[55] ^c
[BiI(S ₂ CNC ₅ H ₁₀) ₂]	piperidine-dtc	III	1D	[53] ^c
[BiI ₂ (S ₂ CNC ₅ H ₁₀)(C ₁₂ H ₁₂ N ₂) ₂]	4-morpholine-dtc	III	1D	[53] ^c

^a Contains a heteroleptic ligand.

^b Bimetallic and contains a bridging halide atom.

^c Includes bridging halide atoms.

^d Contains a co-ligand (non-bridging).

^e Contains a bridging co-ligand.

^f Contains a bridging nitrate counterion.

including materials of higher dimensionalities. These materials are of importance due to their magnetic and conductive properties.

The Kuroda-Sowa group have shown this progressively with various dtc-based ligands and the transition metals Fe [24] and Cu [25,27,28]. They initially produced a series of 1D mixed-valence coordination polymers with Fe [24] and Cu [27,28], which gave rise to materials that showed, respectively, 2D ferroelectric order and

semi-conducting properties with small activation energies. More recently the same group has been able to produce a 3D mixed-valence Cu^I–Cu^{II} CP using the dtc ligand pyrrolidine-dithiocarbamate (Pyr-dtc) [25]. The 3D structure is obtained by infinite Cu(2)-Br chains bridged by mononuclear Cu(Pyr-dtc)₂ units to form a 2D sheet (Fig. 2). Additional Cu(Pyr-dtc)₂ units are then connected to form the 3D network.

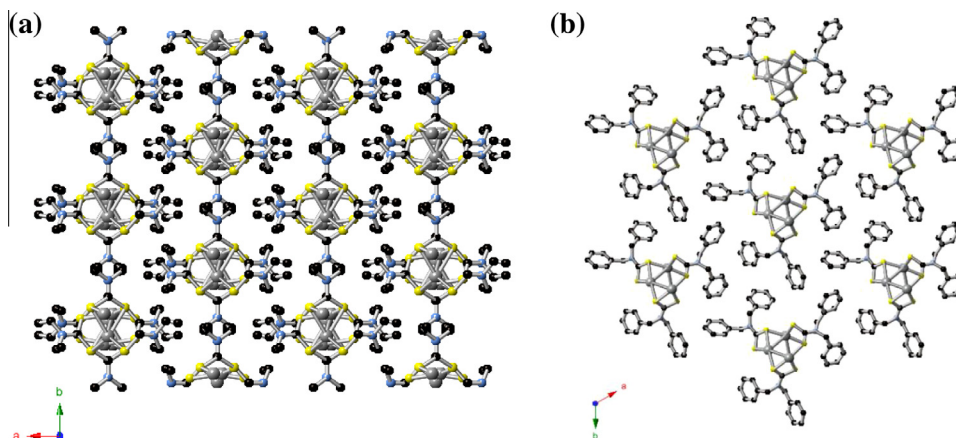


Fig. 1. Dtc-backbone structural packing effects as viewed along *c* axis for (a) $[\text{Ag}(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)]$ with the ligand diethyl-dtc [31] and (b) $[\text{Ag}(\text{S}_2\text{CN}(\text{CH}_2\text{C}_6\text{H}_5)_2)]$ with the ligand dibenzyl-dtc [33] (1D chains going into the page).

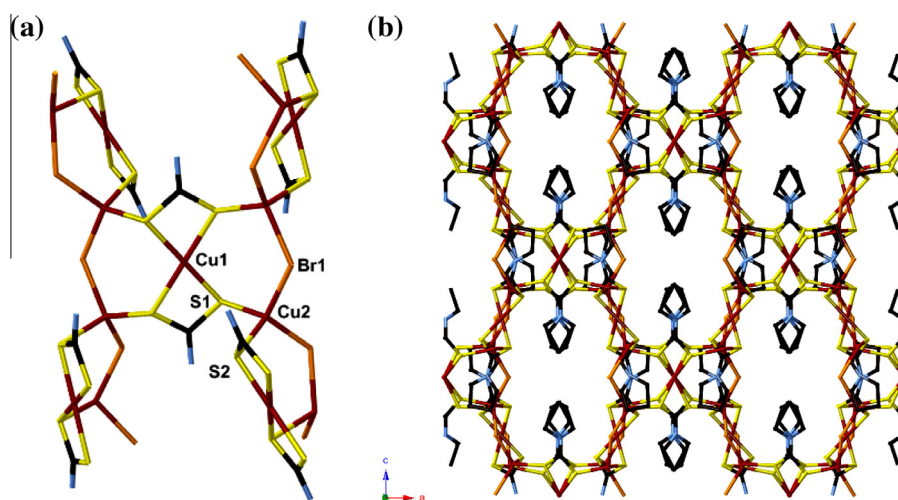


Fig. 2. 3D mixed-valence $\text{Cu}^{\text{I}}-\text{Cu}^{\text{II}}$ coordination polymer produced by Kuroda-Sowa and co-workers [25]. (a) A unit containing five $\text{Cu}(\text{Pyr-dtc})_2$ units and two 1D Cu-Br chains (pyrrolidyl groups and included solvent molecules are omitted for clarity). (b) Sheet structure in the 3D network viewed along *b* axis (hydrogen atoms and included solvent molecules are omitted for clarity).

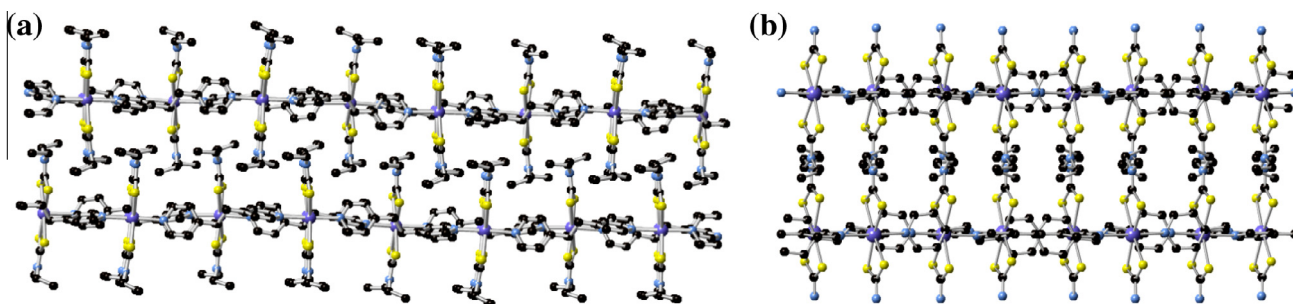


Fig. 3. Packing diagrams of Cd diethyl dtc complexes with the dipyridyl ligands: (a) 1,2-bis(4-pyridyl)ethane [35] viewed along *a* axis and (b) 1,2-bis(4-pyridyl)ethylene [36] viewed along *c* axis.

In addition to the conductive CPs produced by the Kuroda-Sowa group, other research groups have utilised the various coordination modes available to the dtc functional group (Scheme 2), and combined this with bridging halides to produce polymeric complexes. Golding et al. [26] produced more polynuclear Cu-dtc complexes where Cu-Br bridges result in the polymeric complexes $[\text{Cu}(\text{S}_2\text{CNC}_5\text{H}_{10})(\text{CuBr})_4]$ and $[\text{Cu}(\text{S}_2\text{CNC}_5\text{H}_{10})(\text{CuBr})_6]$. Heterobimetallic polymeric dtc complexes have also been synthesised with Rh/Cu and Cr/Cu [18].

2.3. Inclusion of neutral bridging ligands

The polymeric complexes described so far have been obtained from dtc ligands which have not themselves been designed, from a crystal engineering point of view, to produce extended networks. That is, the ligands have been mono-dentate in nature and it has only been through clustering of metal centres and bridging counterions that extended networks have formed. As a result, the CPs produced from these methods exhibit short metal to metal bond

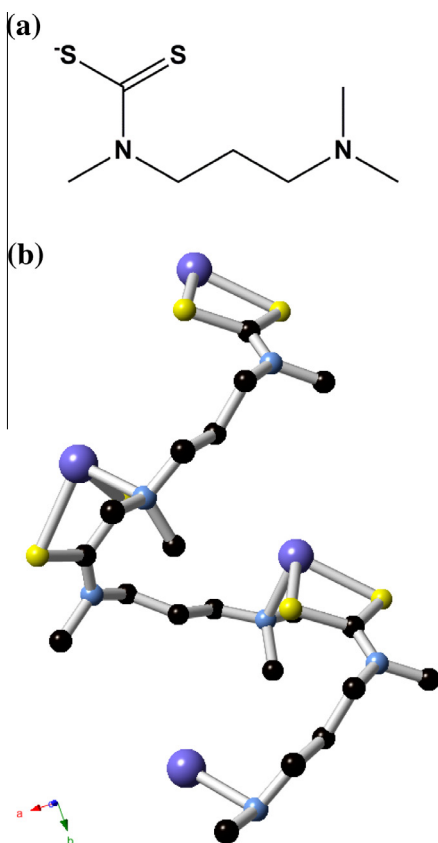


Fig. 4. The helical dtc complex reported by Malik et al. [38]: (a) the heteroleptic ligand, (3-(dimethylamino)propyl)(methyl)-dtc, (b) the 1D helical chain in $[\text{Cd}(\text{S}_2\text{CN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)]$.

distances, and hence, if applicable, small pore sizes. In order to obtain materials that have larger pores due to more spacious packing arrangements, larger bridging co-ligands can be introduced. Teikink and co-workers have shown that multi-ligand systems are feasible, whereby a simple dtc ligand, such as diethyl-dtc, can be reacted with 1,2-bis(4-pyridyl)ethane [35] or 1,2-bis(4-pyridyl)ethylene [36] in the presence of a cadmium salt to give two similar 1D chains (Fig. 3). The chains arise from the di-pyridyl ligands bridging the metal centres and two dtc ligands chelating the metal centre, giving an overall distorted octahedral geometry about the metal atoms. Both chains display the same coordination behaviour however the ethane versus ethylene spacer between the two pyridyl rings of the bridging ligands results in different packing arrangements.

Heteroleptic bridging co-ligands, where a dtc functional group is present at one end of the ligand and another functional group capable of coordinating a metal centre occupies the other end, have also produced a number of polymeric complexes. Malik et al. [38] showed that both Zn and Cd were capable of forming helical 1D chains through coordination with the heteroleptic ligand (3-(dimethylamino)propyl)(methyl)-dtc (Fig. 4). Similarly, Howie et al. [15] showed that a simple alcohol group combined with a dtc functional group produces a heteroleptic ligand which can form a variety of polymeric complexes with the alkaline metals Na, K and Cs. Crystal packing within these complexes is dominated by charge-assisted O–H...S hydrogen bonding, resulting in 3D networks.

Exploration of secondary amine acid analogues with dimethyl tin in presence of CS_2 gave rise to a number of exciting macrocyclic dtc metal complexes with interesting ion-pair recognition which in some instances formed polymeric complexes through interactions between the macrocycles [40]. In addition to these macrocyclic

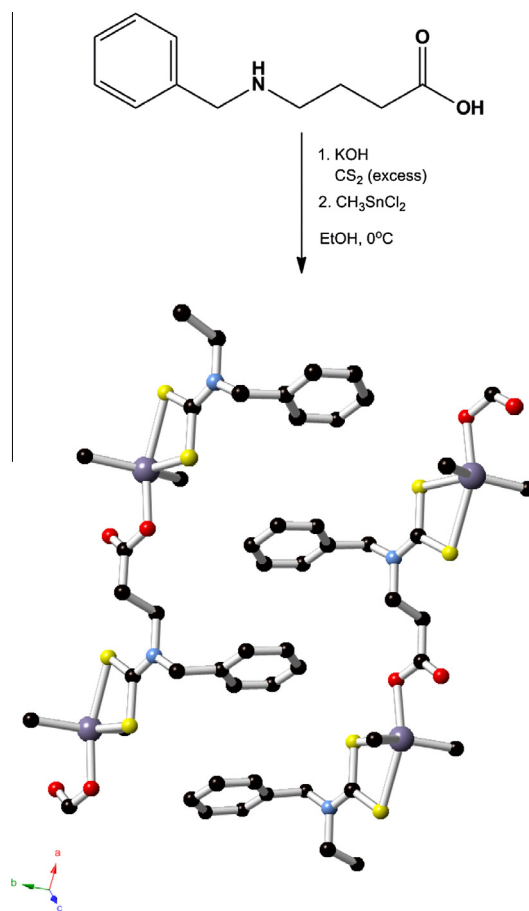


Fig. 5. 1D chain obtained by reaction of *N*-benzyl-3-aminopropionic with dimethyl tin dichloride in an excess of CS_2 .

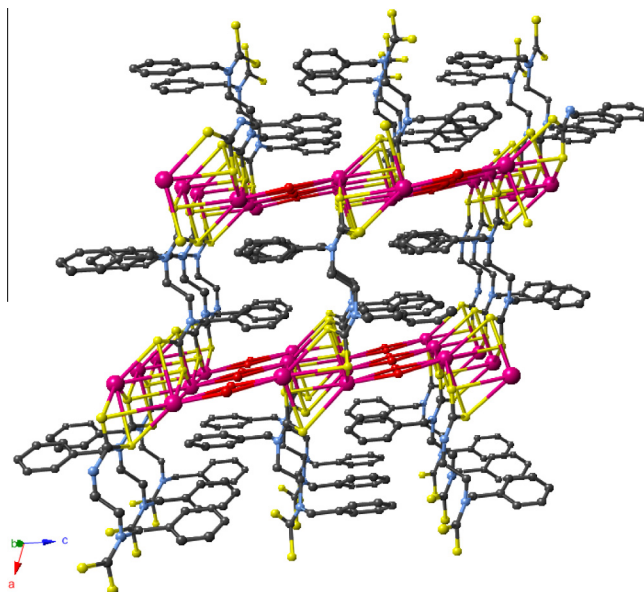
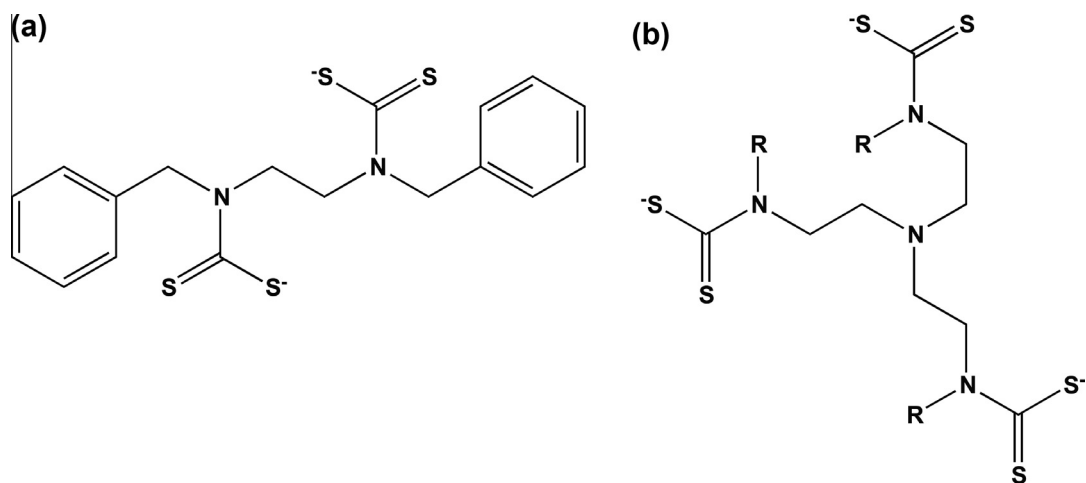


Fig. 6. 3D network, $[\text{M}_2(\text{C}_{18}\text{H}_{18}\text{N}_2\text{S}_4)(\text{H}_2\text{O})]$, formed by reaction of ethane-1,2-diyldis(benzylcarbamodithioate) with M (where M = Rb or Cs) [17].

supramolecular arrays a polymeric chain was produced. The chain was obtained when a mixed dtc and carboxylate ligand was produced *in situ* through reaction of the amino group of the *N*-benzyl-3-aminopropionic ligand with dimethyl tin dichloride in an excess of carbon disulfide (Fig. 5). Both the dtc and carboxylate



Scheme 3. (a) Bis and (b) tris-dtc ligands used by Tlahuext et al. [41] (where R = isopropyl for the polymeric complex).

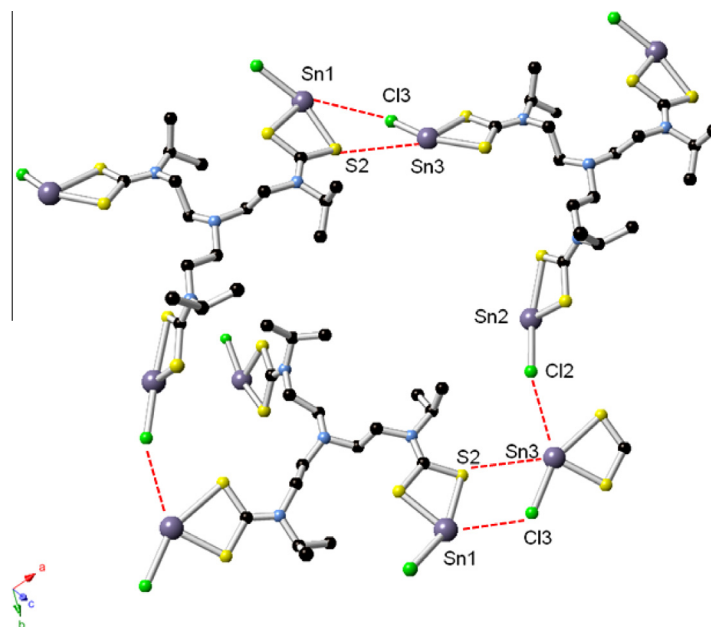
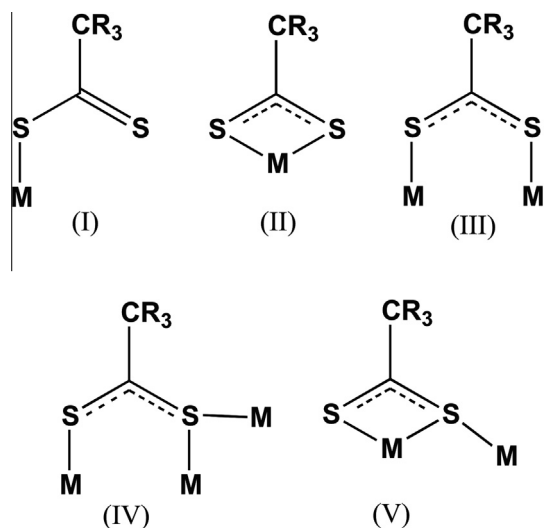


Fig. 7. A 42-membered methylin(IV) tris-dtc macrocycle in the polymeric structure of $[(\text{CH}_3\text{SnCl})_2(\text{N}(\text{CH}_2\text{CH}_2)\text{N}(\text{CH}(\text{CH}_3)_2)\text{CS}_2)]_n$, produced by Tlahuext et al. [41].

groups of the resulting bridging ligand coordinate the metal centres.

In some instances however, only one of the functional groups of the heteroleptic ligand will coordinate. This was the case with the mixed-valence Cu(I)–Cu(II) 1D chain reported by Kim et al. [28], in which the oxygen atom at the other end of the morpholine dtc ligand did not coordinate. Sometimes the inability for both functional groups to coordinate to the metal centre can be related to the preference of a metal for certain donor atoms, such as sulphur (soft) or oxygen (hard). This discrepancy between sulphur donors and both oxygen and nitrogen donors suggests that bis-dtc ligands could be more successful in generating polymeric complexes. However a search of the CSD shows that, to date, there is very little data reported for polymeric bis-dtc metal complexes. There have however been a few examples of bis-dtc salts, such as the K salts reported by Cook et al. [16]. They also report the difficulties of obtaining structural information on transition metal dtc networks due to their extreme insolubility, leading to problems in obtaining suitable crystals for crystallographic analysis. These observations may explain the lack of polymeric bis-dtc-based metal complexes in the CSD.

This issue does not appear to be as prevalent when it comes to the alkaline metals, as a number of bis-dtc alkaline metal salts have been reported with a variety of bis-dtc ligands. The previously mentioned work by Cook et al. [16] contained potassium salts of ethane-1,2-diylbis(methylcarbamdithioate) and the bulkier ethane-1,2-diylbis(isopropylcarbamdithioate). Reyes-Martinez et al. [17] have also shown the various coordination modes available (Scheme 2) when suitable metal centres are bound by bis-dtc ligands, through reaction of the ligand ethane-1,2-diylbis(benzylcarbamdithioate) with Na, K, Rb and Cs. This particular bis-dtc ligand could also be regarded as heteroleptic, because the dtc backbone contains phenyl groups, which are capable of forming cation- π interactions between the alkali metal and the phenyl group. As expected these s-block elements form water-soluble ionic compounds, and the Reyes-Martinez publication shows a trend between the M–O, M–S and cation- π interactions as the size of the metal ion increases from Na to Cs. It was found that the number of water molecules coordinating the metal centre decreased as the ionic radius increased, and the number of coordinating sulphur atoms increased from zero (Na), to two (K) and finally to four (Rb and Cs). The increasing M–S interactions present within the Rb



Scheme 4. Coordination modes of dithiocarboxylate ligands.

and Cs complexes resulted in two isostructural 3D networks forming, as shown in Fig. 6, with the authors attributing these polymeric complexes to a combination of dtc interactions and M– π interactions.

More recently this same research group, as reported by Tlahuext et al. [41], has shown that supramolecular arrays can be obtained from bis-dtc ligands with the main group metal tin. They were able to produce nine new diorganotin(IV) complexes, two with the previously mentioned bis-dtc ligand, ethane-1,2-diylbis(benzylcarbamodithioate) (Scheme 3a), and an additional seven with tris-dtc ligands of the type N(CH₂CH₂N(R)CS₂)₃, where R = CH₃, CH(CH₃)₂ or CH₂C₆H₅ (Scheme 3b). The chloro-dimethyltin bis-dtc complex produced two 1D chain complexes, [(CH₃SnCl)₂(C₆H₅CH₂N(CS₂)CH₂CH₂N(CS₂)CH₂C₆H₅)] and [(CH₃CH₂CH₂CH₂SnCl)₂(C₆H₅CH₂N(CS₂)CH₂CH₂N(CS₂)CH₂C₆H₅)], where in both examples 2D supramolecular arrays are formed through C–H...Cl hydrogen bonds. The tris-dtc ligand, on the other hand, more commonly formed macrocycles which then formed extended supramolecular arrays

through Cl...Sn, Cl...S and C–H...Cl interactions. Of the seven tris-dtc organotin(IV) complexes, the most interesting one is [(Me₂SnCl)₃(tris-dtc-ⁱPr)], due to a 42-membered macrocycle of the composition [C₁₈Cl₄N₉S₆Sn₅] forming through additional intermolecular forces (Cl...Sn, Cl...S and C–H...Cl) resulting in a 3D array (Fig. 7).

3. Dithiocarboxylates

Dithiocarboxylates, or dithiolates as they are sometimes referred, are the sulphur analogues of carboxylates. As observed with the dtc ligands, the larger ionic radius of the sulphur atom again allows for an increased number of sulphur-metal bonds, resulting in a range of high coordination numbers between ligand and metal (Scheme 4). Review of the literature shows 66 of 709 (ca. 8%) crystallographically characterised dithiocarboxylates in the CSD [14] are polymeric. When compared to dtc complexes, however, there are significantly less as a whole (2475 dtc versus 709 dithiocarboxylate complexes).

Detailed analysis of polymeric dithiocarboxylate complexes (Table 2) reveals that there is less variation within the complexes compared to the dtc complexes. There are fewer metals incorporated into such complexes with the vast majority (ca. 88%) being formed with Ni [57–58] and Pt [62,63,65–70], although there are a few other examples, such as Li [56], Zn [59], Au [71,72], Ag [61], and Sn [73]. Schuerman et al. [71] produced a 1D polymer containing gold hexameric subunits with the ligand *o*-methylthiobenzato. The six Au atoms of the [Au₆(S₂C-*o*-C₆H₄CH₃)₆] complex are coplanar to within 0.14 Å, with each ligand bridging neighbouring Au atoms such that they lie alternatively above and below the plane (Fig. 8a). The Au hexamer units are then linked by Au–Au bonds between Au(3) and Au(6), resulting in a linear polymeric 1D chain (Fig. 8b).

Gallego et al. [72] also produced a 1D Au CP with the ligand isopentanedithiolato, where bridging dithiocarboxylato ligands give rise to the formation of the 1D chains. The Ag dithiolate complex reported by Lanfredi et al. [61] was a tetranuclear complex, with the metal centres bridged by the dithiolate ligand dithio-*o*-toluato. Each Ag atom interacts with a nearby Ag centre and four sulphur atoms from four ligands, with each sulphur atom acting

Table 2
Dithiocarboxylate complexes.

Complex	S-ligand	Coordination mode	Dimensionality	Refs.
Li(2-CH ₃ C ₄ H ₂ N ₂)CH ₂ CS ₂ ·TMEDA	3-methylpyrazine-2-carbodithioate	III	1D	[56]
[Ni ₂ (CH ₃ CS ₂) ₄]	methylthioacetato	II	1D	[57] ^a
[Ni ^{II}] ₂ (CH ₃ CH ₂ CS ₂) ₄]	ethylthioacetato	II	1D	[58] ^{a,b}
[Ni ^{II}] ₂ (CH ₃ (CH ₂) ₂ CS ₂) ₄]	propylthioacetato	II	1D	[58] ^{a,b}
[Ni ^{II}] ₂ (CH ₃ (CH ₂) ₃ CS ₂) ₄]	butylthioacetato	II	1D	[58] ^{a,b}
[Zn(S ₂ CC ₆ H ₄ CS ₂)(DMF) ₂].DMF	benzene-1,4-bis(carbodithioate)	III	1D	[59] ^c
[Pd ₂ (CH ₃ CS ₂) ₄]	methylthioacetato	II	1D	[60] ^d
[Ag(S ₂ C- <i>o</i> -C ₆ H ₄ CH ₃) ₄]	2-methylbenzodithioate	IV	1D	[61]
[Pt ^{II}] ₂ (CH ₃ CS ₂) ₄]	methylthioacetato	II	1D	[62–63] ^a
[Pt ^{II}] ₂ (CH ₃ CS ₂) ₄]	methylthioacetato	II	1D	[64] ^{a,b}
[Pt ₂ (CH ₃ CS ₂) ₄]	methylthioacetato	II	1D	[65] ^d
[Pt ₂ (CH ₃ CH ₂ CS ₂) ₄]	ethylthioacetato	II	1D	[65] ^d
[Pt ^{II}] ₂ (CH ₃ CH ₂ CS ₂) ₄]	ethylthioacetato	II	1D	[66] ^{a,b}
[Pt ₂ ((CH ₃) ₂ CHCS ₂) ₄]	2-methylpropanedithioate	II	1D	[67] ^d
[Pt ^{II}] ₂ (CH ₃ (CH ₂) ₃ CS ₂) ₄]	<i>n</i> -but-carbodithioate	II	1D	[68] ^{a,b}
[Pt ^{II}] ₂ (CH ₃ (CH ₂) ₄ CS ₂) ₄]	<i>n</i> -pen-carbodithioate	II	1D	[69] ^{a,b}
[Pt ₂ (C ₆ H ₅ CH ₂ CS ₂) ₄]	phenylthioacetato	II	1D	[70] ^d
[Au ₆ (S ₂ C- <i>o</i> -C ₆ H ₄ CH ₃) ₆]	2-methylbenzodithioate	II	1D	[71] ^d
[Au ₂ (S ₂ CCH ₂ CH(CH ₃) ₂) ₂]	3-methylbutanedithioate	II	1D	[72] ^d
[(CH ₃) ₂ Sn(S ₂ CC ₃ H ₂ N ₂)]	4(5)-imidazoledithiocarboxylate	I	1D	[73] ^e

^a Includes bridging halide atoms.

^b More than one data set for this compound (collected at various temperatures).

^c Bridging bis-dithiolate ligand, with ligand having an overall coordination mode of μ_2 - $\kappa^1, \kappa^1, \kappa^1, \kappa^1$.

^d Additional M–M interactions give rise to 1D chains.

^e Contains a heteroleptic ligand.

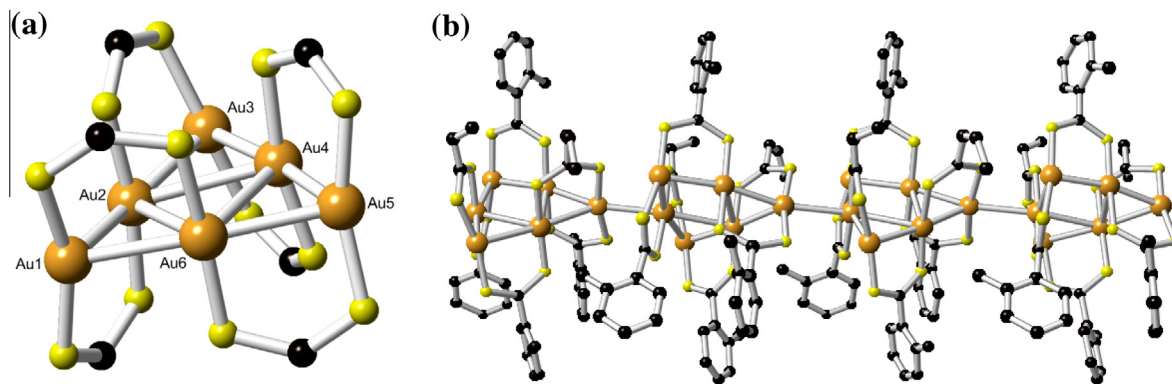


Fig. 8. The 1D gold hexamer chain, $[\text{Au}_6(\text{S}_2\text{C}-o\text{-C}_6\text{H}_4\text{CH}_3)_6]$, produced by Schuerman et al. [71]. (a) Gold hexamer unit (methylbenzene omitted for clarity). (b) Gold hexamer units linked by additional Au–Au bonds between Au(3) and Au(6) producing a 1D chain, as viewed along the *b* axis.

as a bidentate donor between two metal centres, resulting in a 1D chain. Packing of the dithiolate linked chains is influenced by edge-to-face π - π interactions between toluene groups of adjacent chains.

In terms of useful physical properties the most interesting and heavily explored structures have been with the d^8 metals Ni^{II} , Pd^{II} and Pt^{II} . Initial studies by Bellitto et al. [70,74] showed that polymeric compounds of the type $[\text{M}(\text{RCS}_2)_4]$ ($\text{M} = \text{Pt}^{\text{II}}$, Pd^{II} or Ni^{II} , $\text{R} =$ aliphatic group) can be prepared, and that such materials show anisotropic physical properties. The polymeric 1D chains obtained are similar for a number of aliphatic groups, with metal dimers coordinating four dithiolate based ligands around each metal centre, giving approximately square-planar chromophores that stack along a two-fold axis; M–M interactions between chromophores generate the polymeric chain. While investigating these compounds, Bellitto and co-workers [62,63,67] found that Pt readily undergoes oxidative addition with halogens to give $[\text{Pt}(\text{RCS}_2)_4\text{I}_2]$ ($\text{R} =$ aliphatic group). As was observed previously, the dithiolate linked metal dimers give rise to square-planar $[\text{Pt}_2\text{S}_8]$ chromophores, but now these chromophores are linked by halides, and subsequently stacked to give 1D CPs. The Pt–Pt distance in the dimer is 2.677(3) and the Pt–I distances are 2.975(1) and 2.981(3) either side of the dimeric $[\text{Pt}_2\text{S}_8]$ species resulting in a near symmetrical M–I–M bridge. As a result these materials exhibit interesting semi-conducting properties, with an exponential temperature dependence. Bellitto and co-workers have also produced a similar halogen reduced compound with Ni, $[\text{Ni}_2(\text{CH}_3\text{CS}_2)_4\text{I}]$ [57], for which semiconducting properties were observed, and this observation has since been classified as Mott–Hubbard semiconductivity [75].

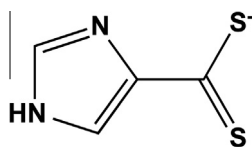
This system has since been further explored by Mitsumi et al. [58,65,66,68,69] and Kitagawa et al. [64], with the structural changes observed within these mixed-valence binuclear MMX chains (as they are commonly referred) investigated at various temperatures. The low temperature crystallographic investigations have given a deeper understanding into the exponential temperature dependence in semiconducting properties. In particular, the nature of the various structural modifications brought about by the metal-semiconducting transition was examined in detail, with a notable effect caused by sudden and drastic increases in Pt–I distances observed near the transition temperature (205 K). Mitsumi

et al. [66] observed these changes by examining the crystal structure of $[\text{Pt}_2(\text{C}_2\text{H}_7\text{CS}_2)_4\text{I}]$ at five different temperatures, three below and two above the transition temperature. Kitagawa et al. [64] conducted similar temperature crystallographic studies on the 1D chain $[\text{Pt}_2(\text{CH}_3\text{CS}_2)_4\text{I}]$. These two Pt mixed-valence halogen bridged 1D complexes are usually in the class II mixed-valence state and show shifts in the halogen distances due to Peirels transitions. Nickel compounds, on the other hand, tend to be in a class III averaged-valence state where strong electron–electron correlation of the Ni atoms allows these materials to be classified as Mott–Hubbard semiconductors, as had been shown previously by Bellitto and co-workers. Mitsumi et al. [58] were again able to expand on the work initiated by Bellitto and co-workers by producing a series of $[\text{Ni}^{\text{II/III}}_2(\text{RCS}_2)_4\text{I}]$ compounds where the R group was varied in length. Three compounds were synthesised where the R group was varied from a simple ethyl, to the longer *n*-propyl and *n*-butyl groups. Analysis of these compounds at low temperatures showed that they exhibit markedly different magnetic behaviour, and the authors also found that elongation of the alkyl chain of the dithiocarboxylate ligand affected the ability of the complex to adopt twofold periodic valence ordering and subsequently affects the magnetic susceptibility.

3.1. Inclusion of bidentate ligands

Up to this point 46 of the 53 crystallographically studied complexes have been based on $[\text{M}(\text{RCS}_2)_4]$ and $[\text{M}(\text{RCS}_2)_4\text{I}]$ where differences between metals, R groups and/or the temperature at which they were collected lead to subtle changes in the overall configuration of the 1D chains. While these subtle differences lead to vastly different properties of the materials, especially in relation to their capabilities as conductive materials, it also results in less variation in terms of structural features. There are, however, three polymeric dithiolate complexes which differ significantly to those already discussed. These polymers involve the use of the heteroleptic ligands 3-methylpyrazine-2-carbodithioate and 4(5)-imidazoledithiocarboxylic acid, and another polymeric complex synthesised from the dipiperidinium salt of the tetrathioterephthalate dianion, $(\text{C}_5\text{H}_{10}\text{NH}_2)_2(\text{S}_2\text{CC}_6\text{H}_4\text{CS}_2)$.

The first heteroleptic ligand, 3-methylpyrazine-2-carbodithioate, forms a 1D chain with the alkaline metal Li and was reported by Ball et al. [56]. At the time, the Li–dithiocarboxylate complexes reported in this paper were the only ones of their kind, however since this publication there have been additional dithiolate Li based dithiocarboxylate clusters/monomers reported, but no polymeric complexes. The twisted 1D chain of $(2\text{-CH}_3\text{C}_4\text{H}_2\text{N}_2)\text{CH}_2\text{CS}_2\text{Li-TMEDA}$ (where TMEDA = tetramethylethylenediamine) contains a five-coordinate Li centre, which has both sulphur atoms of the dithiolate



Scheme 5. Heteroleptic ligand used by Ma et al. [73], 4(5)-imidazoledithiocarboxylate.

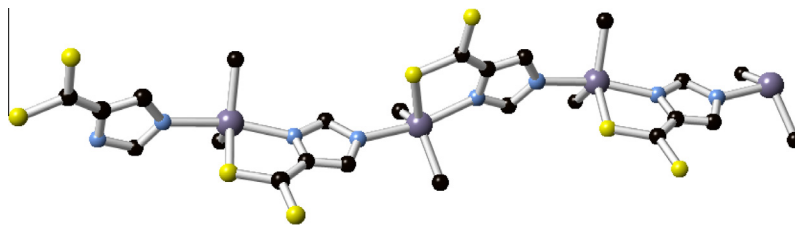


Fig. 9. Fragment of the 1D chain produced by Ma et al. [73] showing the coordination mode adopted by the 4(5)-imidazoledithiocarboxylate ligand.

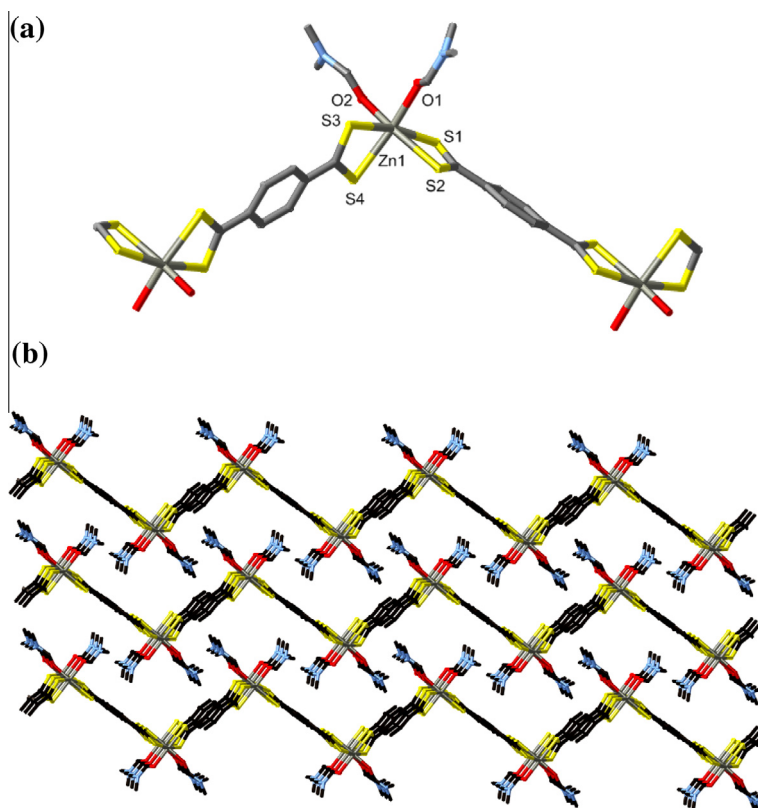


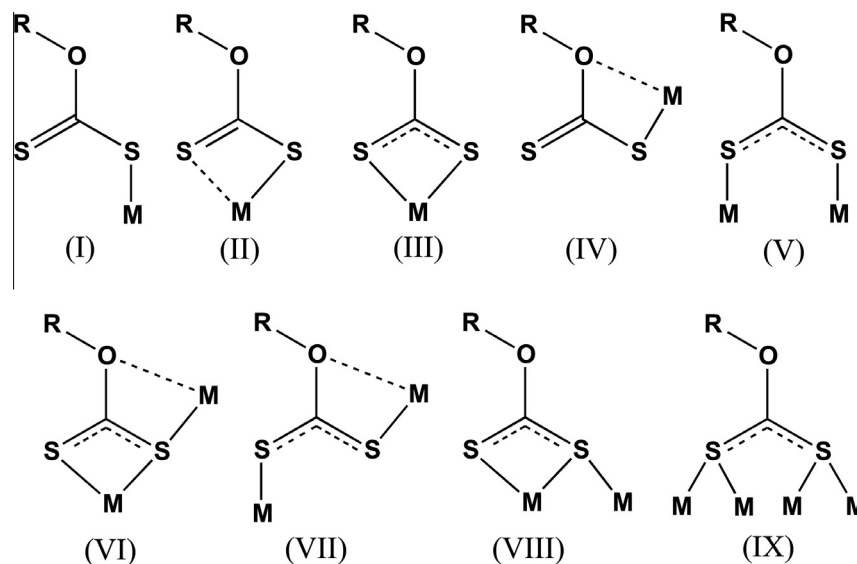
Fig. 10. 1D chain $[Zn(S_2CC_6H_4CS_2)(DMF)_2] \cdot DMF$ [59]: (a) Coordination environment of the Zn atoms. (b) View looking down the a axis. (H atoms and lattice DMF molecules omitted for clarity).

coordinating, as well as the N from the pyrazine (N ortho to the attached methyl) of an adjacent monomer, giving a polymeric network. The additional coordination sites around the Li centre are occupied by two N atoms of a chelating TMEDA ligand.

The second heteroleptic ligand, 4(5)-imidazoledithiocarboxylate (Scheme 5), has been incorporated into a dimethyltin(IV) polymeric complex by Ma et al. [73]. They describe the 4(5)-imidazoledithiocarboxylic ligand as multidentate, where the coordination possibilities include the deprotonated thiol as well as active nitrogen atoms of the imidazole. The combination of various organotin(IV) dichlorides with this heteroleptic ligand gave rise to 12 novel complexes showing a range of coordination modes, however only one of these complexes was polymeric. In the complex $[(CH_3)_2Sn(S_2CC_3H_2N_2)]$ the 4(5)-imidazoledithiocarboxylate ligand chelates the metal centre through one of the sulphur atoms of the dithiocarboxylate and the nitrogen of the imidazole; an additional Sn–N interaction between the other nitrogen atom of the heteroleptic ligand produces the 1D chain (Fig. 9). There are no strong interactions between the chains, resulting in a less structured packing arrangement in which pairs of 1D chains run perpendicular to each other and parallel to the diagonals of the bc plane.

The final dithiocarboxylate based CP to be discussed is an interesting one, as it is the only crystallographic example of a CP containing a bridging bis-dithiolate ligand. The 1D chain produced by Neofotistou et al. [59] resulted from the reaction of Zn with the bis-dithiocarboxylate dianion, tetrathioterephthalate ($tttp^{2-}$). The $tttp^{2-}$ ligand is the sulphur analogue of the heavily explored terephthalic acid (or 1,4-benzenedicarboxylic acid). This interesting choice of ligand, with its rigid structure and its ability to bridge through linear placement of the coordination sites, is an ideal ligand for formation of CPs. The 1D CP produced by Neofotistou [59] has DMF solvated metal centres bridged by two $tttp$ ligands, with the overall geometry of the metal centre being a highly distorted octahedral environment (Fig. 10a). The chelating dithiolate groups of the two $tttp$ ligands occupy four of the coordination sites of the distorted octahedral arrangement with the last two occupied by oxygen atoms from the coordinated DMF molecules. The two $tttp$ ligands are arranged in such a way that infinite zigzag chains are produced, as shown in Fig. 10b.

This material was found to possess interesting optoelectronic properties, and also demonstrates that dithiocarboxylate based CPs are possible with bis-dithiolate ligands. As was reported with



Scheme 6. Some of the coordination modes available to the xanthate ligand.

Table 3
Xanthate Complexes.

Complex	S-ligand	Coordination mode	Dimensionality	Refs.
[Ba(S ₂ COCH ₂ CH ₃) ₂]	ethyl xanthate	VI	2D	[76] ^a
[Ni(S ₂ COCH ₂ CH ₃) ₂ (C ₁₀ H ₈ N ₂)]	ethyl xanthate	III	1D	[77] ^b
[Ni(S ₂ COCH(CH ₃) ₂) ₂ (C ₄ H ₄ N ₂)]	isopropyl xanthate	III	1D	[78] ^c
[Ni(S ₂ COCH(CH ₃) ₂) ₂ (C ₁₂ H ₁₂ N ₂)]	isopropyl xanthate	III	1D	[79] ^d
[Ni(S ₂ COCH ₂ CH ₂ CH ₂ CH ₃) ₂ (C ₁₀ H ₈ N ₂)]	butyl xanthate	III	1D	[80] ^b
[Ni(S ₂ COC ₁₁ H ₁₇)(C ₁₀ H ₈ N ₂)]	bis- <i>o</i> -boronyl xanthate	III	1D	[81] ^b
[Zn(S ₂ COCH ₂ CH ₃) ₂]	ethyl xanthate	V		[82]
[Zn(S ₂ COCH ₂ CH ₃) ₂ (C ₁₂ H ₁₂ N ₂)]	ethyl xanthate	I	1D	[83] ^d
[Zn(S ₂ COCH ₂ CH ₃) ₂ (C ₄ H ₄ N ₂)]	ethyl xanthate	III	1D	[84] ^c
[Zn(S ₂ COCH ₂ CH ₂ CH ₂ CH ₃) ₂ (C ₁₂ H ₁₂ N ₂)]	butyl xanthate	I	1D	[83] ^d
[Ag(S ₂ COCH ₂ CH ₃)]	ethyl xanthate	IX	2D	[85]
[Cd(S ₂ COCH ₃) ₂]	methyl xanthate	VIII	1D	[86]
[Cd(S ₂ COCH ₂ CH ₃) ₂]	ethyl xanthate	V	2D	[87]
[Cd ₂ (S ₂ COCH(CH ₃) ₂) ₃]	isopropyl xanthate	VIII	2D	[88] ^a
[Cd(S ₂ COCH(CH ₃) ₂) ₂]	isopropyl xanthate	V	2D	[89]
[Cd(S ₂ COCH(CH ₃) ₂) ₂ (C ₁₀ H ₈ N ₂)]	isopropyl xanthate	III	1D	[90] ^b
[Cd(S ₂ COCH ₂ CH ₂ CH ₂ CH ₃) ₂]	butyl xanthate	V	2D	[91]
[Sb(S ₂ COCH ₂ CH ₃) ₂ Br]	ethyl xanthate	III	1D	[92] ^a
[Hg(S ₂ COCH ₃) ₂]	methyl xanthate	IV and VII	1D	[93]
[Hg(S ₂ COCH ₂ CH ₃) ₂]	ethyl xanthate	VII	2D	[94–95]
[Hg(S ₂ COC(CH ₃) ₂) ₂]	isopropyl xanthate	VIII	2D	[96]
[Hg(S ₂ COCH ₂ CH ₂ CH ₂ CH ₃) ₂]	butyl xanthate	VII	2D	[97]
[Hg(S ₂ COCH ₂ CH ₂ CH ₂ C(CH ₃) ₃) ₂]	(3,3-dimethylbutyl) xanthate	V	2D	[97]
[Hg(S ₂ COCH ₂ CH ₂ CH ₂ CH ₂ CH ₃) ₂]	pentyl xanthate	V	2D	[97]
[Hg(S ₂ COCH ₂ CH ₂ CH ₂ C(CH ₃) ₂) ₂]	isopentyl xanthate	V	2D	[97]
[Pb(S ₂ COCH ₃) ₂]	methyl xanthate	VIII	1D	[98]
[Bi(S ₂ COCH(CH ₃) ₂) ₃]	isopropyl xanthate	III and VIII	1D	[99–100]

^a Includes bridging halide atoms.

^b Contains bridging co-ligand (4,4'-bipyridine).

^c Contains bridging co-ligand (pyrazine).

^d Contains bridging co-ligand (1,2-di-4-pyridylethane).

dtc complexes, however, there appears to be some challenging synthetic hurdles to be overcome in regards to such materials.

4. Xanthates

Variation in binding motif is also observed with xanthates (Scheme 6), with the variation in coordination modes arising from both the sulphur atoms as well as the oxygen atom of the xanthate functional group being capable of forming coordination bonds. A few of these coordination modes are rare, while others are more commonly observed, as outlined in Table 3.

The first polymeric xanthate complex cadmium *n*-butyl xanthate, [Cd(S₂COC₄H₉)₂], was reported by Rietveld and Maslen in 1965 [91]. In this complex the central Cd atom is surrounded by four sulphur atoms in an almost tetrahedral environment (Fig. 11a). Each sulphur atom coordinated to the Cd atom is from a different xanthate ligand, i.e. the xanthate ligands are bridging (M–S–C–S–M) between two metal centres, resulting in a 2D sheet (Fig. 11b). A year after this complex was reported a zinc ethyl xanthate, [Zn(S₂COC₂H₅)₂], was published by Ikeda and Hagihara [82]. While the shorter xanthate ligand, ethyl as opposed to *n*-butyl, means the overall packing is different, both metals produce com-

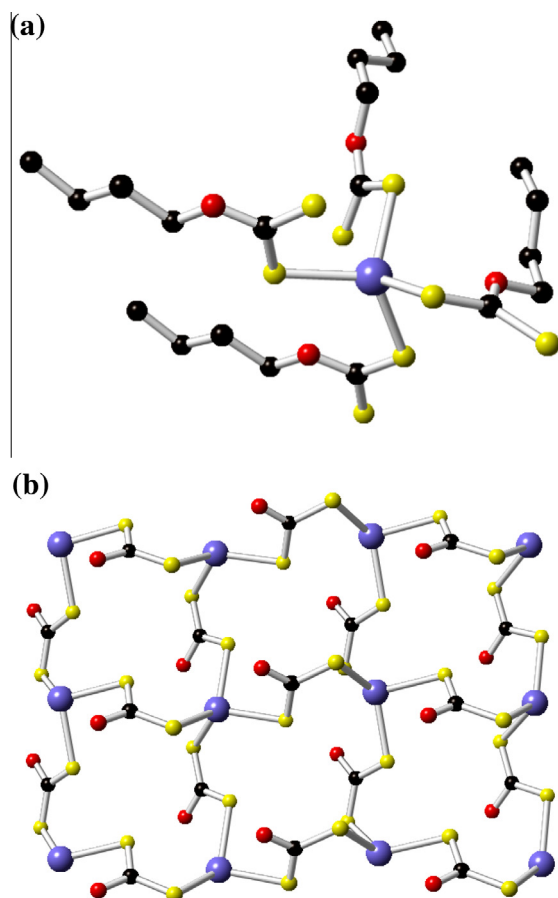


Fig. 11. First polymeric xanthate complex, $[\text{Cd}(\text{S}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]$, reported by Rietveld and Maslen: (a) Coordination about the metal centre and (b) 2D sheet formed by bridging xanthate ligands (alkyl chain backbone from O of xanthate ligand has been omitted for clarity).

plexes with the same bridging mode of the xanthate ligand (mode V, Scheme 6), giving rise to a two-dimensional structure, where 16-membered tetrameric rings form between four metal centres, similar to that observed with the Cd complex shown in Fig. 11b. Since these first two polymeric species were published numerous Cd [87,89], Hg [96–97] and Zn [82] structures have been reported to contain similar 2D sheets, with the alkyl chain length resulting in slightly different packing arrangements.

Whilst numerous xanthate complexes, with a variety of metals and alkyl chain lengths, have produced this same 2D motif (Table 3), it is not the only structural type observed. Various reports on Hg xanthate complexes have shown that the alkyl group of the xanthate can play a crucial role in deciding the overall structure of the complex. When considering complexes of the form $[\text{Hg}(\text{S}_2\text{COR})_2]$, when R = ethyl [94–95], 3,3-dimethylbutyl [97] or *n*-pentyl [97], the previously mentioned 2D structure is attained. A similar motif is also observed for $[\text{Hg}(\text{S}_2\text{COR})_2]$, when R = isopropyl [96], *n*-propyl [101] and *n*-butyl [97], however in the case of isopropyl xanthate, two of the four metal centres in each 16-membered ring are five-coordinate due to an additional bond forming between the metal centre and an oxygen atom from the xanthate ligand. The *n*-propyl and *n*-butyl complexes also give similar 2D sheets, but in these two complexes all of the metal centres are six-coordinate with both the sulphur atoms and the oxygen atom of each xanthate ligand coordinating. In all these complexes the bulkiness of the alkyl groups affects the overall packing either through steric hindrance or through intermolecular interactions. The alkyl derivative which gave the greatest degree

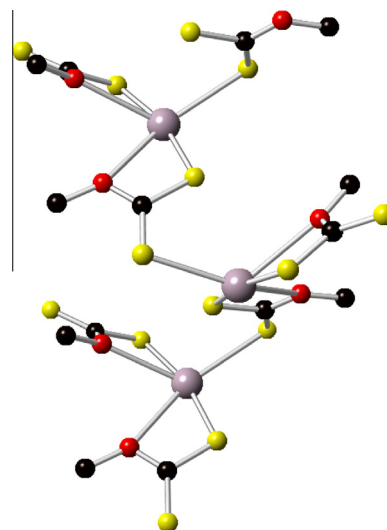


Fig. 12. Helical 1D chain, $[\text{Hg}(\text{S}_2\text{COCH}_3)_2]$, formed from reaction of Hg with methyl xanthate [93].

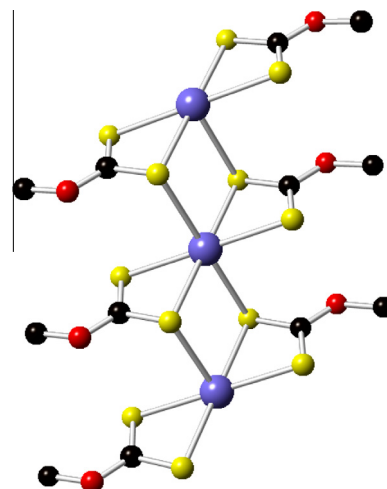


Fig. 13. 1D staggered chain observed in $[\text{Cd}(\text{S}_2\text{COCH}_3)_2]$ by Young Jr. et al. [86].

of difference, however, was the small methyl xanthate [93], where the 2D network is no longer observed and a linear 1D chain forms instead. The small and sterically unhindered methyl xanthate allows the metal centre to be five-coordinate, where three sulphur atoms and two oxygen atoms bond to the metal centre. The two sulphur atoms come from two different xanthate ligands, with one of the ligands binding in a monodentate fashion and the other sulphur atom not participating in any coordination, or any significant intermolecular interactions. The second xanthate ligand has both sulphur ligands coordinating to two different metal centres in the M–S–C–S–M bridging mode (mode V, Scheme 4) seen previously, giving a helical polymeric chain (Fig. 12).

A similar story between differing alkyl chains can be seen with Cd xanthate complexes, whereby the xanthate ligands bridge to give the commonly observed 2D structure discussed above, with the alkyl groups ethyl [87], isopropyl [89] and the previously mentioned *n*-butyl [91]. As was observed with Hg, when using the smaller methyl xanthate a 1D chain is observed, however the 1D chain for the Cd derivative is significantly different to the Hg one. The cadmium methyl xanthate complex by Young Jr. et al. [86] is a linear 1D chain, where each metal centre is surrounded by six sulphur atoms, four of these from two chelating xanthate li-

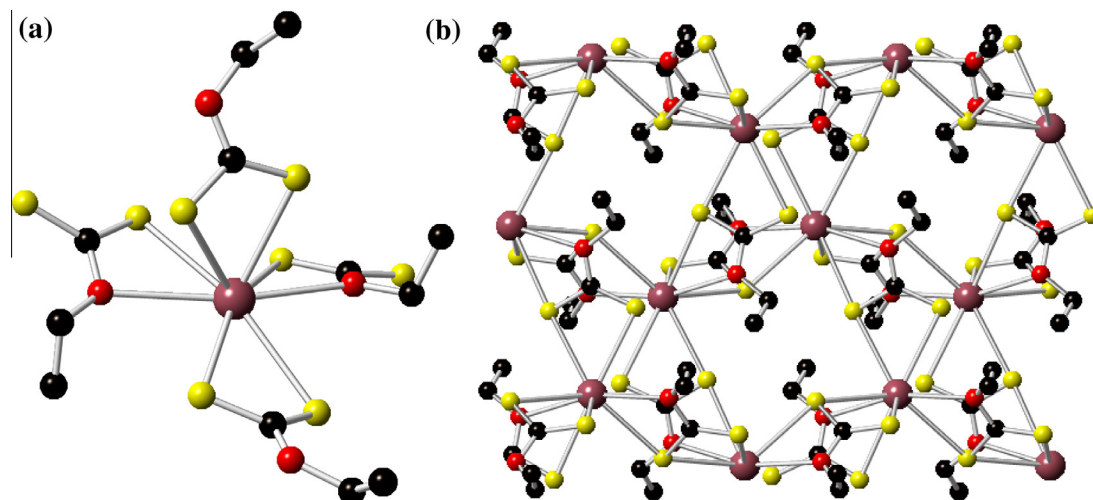


Fig. 14. The $[\text{Ba}(\text{S}_2\text{COCH}_2\text{CH}_3)_2]$ complex published by Bezougli et al. [76]: (a) eight-coordinate metal centre and (b) packing of a single 2D sheet, as viewed along the a axis.

gands giving a square planar arrangement. These molecules then associate in the crystal structure via Cd–S interactions above and below the square plane, as shown in Fig. 13.

Other polymeric xanthate complexes have been obtained with the metals Tl [102], Pb [98], Bi [99,100] and Ba [76]. The larger ionic radius of these metals allows for more xanthate ligands to coordinate around the central metal atom. For example in the Pb methyl xanthate complex $[\text{Pb}(\text{S}_2\text{COCH}_3)_2]$ [98] the Pb atom has two chelating xanthate ligands coordinating through the two sulphur atoms of the ligands. In addition one sulphur atom from each ligand also coordinates to an adjacent Pb centre, resulting in a six-coordinate metal centre and generating a linear polymer. Increasing the ionic radius to Bi allows for greater coordination numbers about the central metal. Hoskins et al. [100] synthesised a seven-coordinate Bi isopropyl xanthate complex, $[\text{Bi}(\text{S}_2\text{COC}_3\text{H}_7)_3]$. In this example each Bi metal centre is bonded to three bidentate xanthate ligands, two of which chelate the metal centre, while the third displays significant asymmetry due to an additional bond to a neighbouring Bi atom, which leads to a linear polymeric chain. Bezougli et al. [76] showed that Ba is also capable of coordinating an increasing number of xanthate ligands with the simple ligand ethyl xanthate leading to four ligands around the metal in the structure of $[\text{Ba}(\text{S}_2\text{COCH}_2\text{CH}_3)_2]$ (Fig. 14a). Each metal centre has two xanthate ligands chelating the metal centre through the two sulphur atoms, and two xanthate ligands which link through a bidentate mode via a sulphur atom and the oxygen donor of the xanthate ligand, resulting in a 2D sheet (Fig. 14b).

The ability of xanthate ligands to bridge metal centres means that there are fewer examples in the literature with bridging counterions, such as halides, than were seen with both the dtc and dithiocarboxylate ligands. There are, however, some examples, such as the iodide bridged Cd isopropyl xanthate complex prepared by Abrahams et al. [88]. While inclusion of halogen atoms to bridge metal centres is not uncommon in the greater scope of metal xanthate complexes, this $[\text{Cd}_2\text{I}(\text{S}_2\text{COCH}(\text{CH}_3)_2)_3]$ complex is one of only two examples of polymeric complexes. As expected the iodine atoms bridge between two metal centres, however there are two different metal environments present in this complex. The Cd(1) metal centre, which has the iodine bridges, is six-coordinate with two bonds occupied by the bridging iodines and an additional four bonds to two chelating xanthate ligands (Fig. 15a). These xanthate ligands then form an additional bond from one of the sulphur atoms to the Cd(2) centre, which is five-coordinate. An additional chelating xanthate ligand, with the coordination mode VIII (Scheme 6), is observed where one of the sulphur atoms from this ligand bonds to an adjacent Cd(2) atom, giving the fifth coordination site (Fig. 15b). These coordination modes result in 16-membered $\text{Cd}_8\text{S}_6\text{I}_2$ rings which give a 2D network (Fig. 16). The other halide example contains a bromide bridge between Sb metal centres to produce the 1D chain $[\text{Sb}(\text{S}_2\text{COCH}_2\text{CH}_3)_2\text{Br}]$ [92]. This complex contained the same ethyl xanthate as that used in the iodine bridged Cd xanthate complex above, however differing metal properties result in the Sb coordinating only two xanthate ligands. Both xanthate ligands chelate the metal centre, and as such the single Sb–Br links give rise to the polymeric chain.

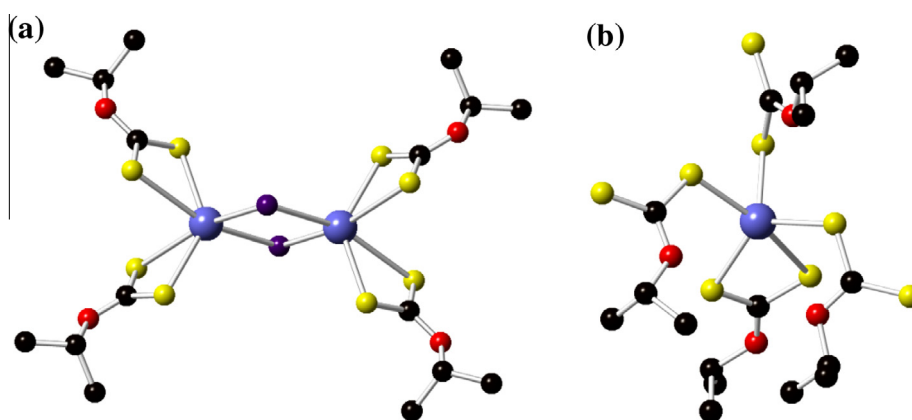


Fig. 15. Coordination environments for both Cd metal centres in $[\text{Cd}_2\text{I}(\text{S}_2\text{COCH}(\text{CH}_3)_2)_3]$ [88]: (a) six-coordinate Cd1 and (b) five-coordinate Cd2.

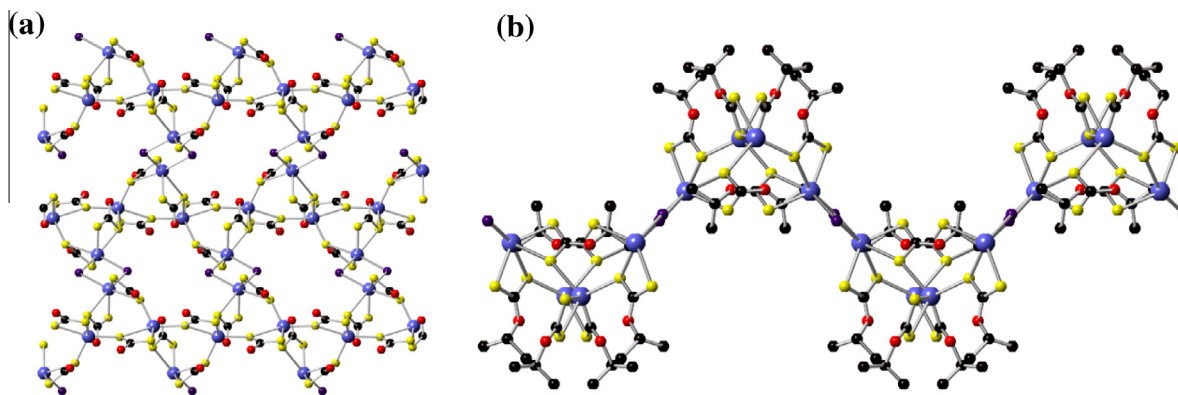


Fig. 16. A single 2D sheet of $[\text{Cd}_2(\text{S}_2\text{COCH}(\text{CH}_3)_2)_3]$ [88]: (a) 16 membered $\text{Cd}_6\text{S}_6\text{I}_2$ rings can be viewed along a axis and (b) 2D sheet viewed along the c axis.

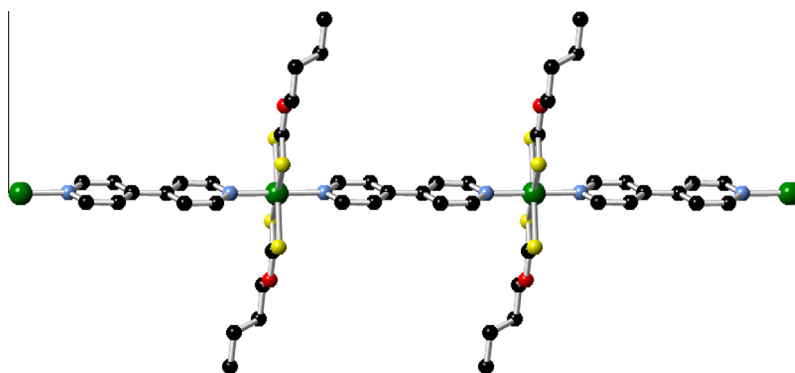


Fig. 17. Linear chains produced by the *trans* arrangement of 4,4'-bipyridine ligands in the complex $[\text{Ni}(\text{S}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$ [80].

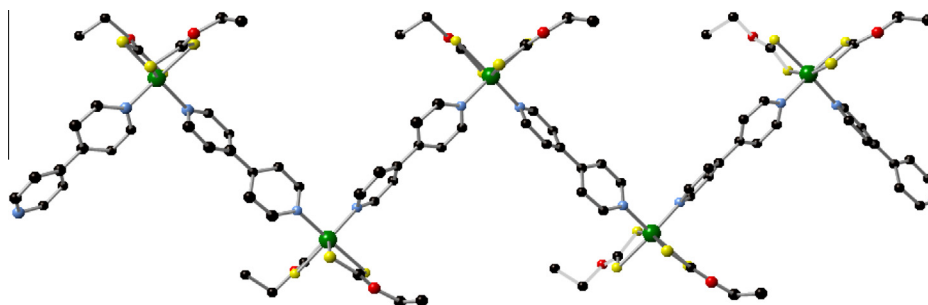


Fig. 18. Zigzag chain produced by the *cis* arrangement of 4,4'-bipyridine ligands in the complex $[\text{Ni}(\text{S}_2\text{COCH}_2\text{CH}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$ [77].

4.1. Inclusion of bidentate ligands

As has been observed with both dtc and dithiocarboxylate based complexes, one of the most successful and reliable ways of producing polymeric species with greater distances between metal centres is through the inclusion of bridging co-ligands. Again despite competition between hard and soft donor atoms, three different N-donor ligands have been successfully incorporated into xanthate containing polymeric complexes.

The three bridging co-ligands 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethylene and pyrazine have successfully been incorporated into various metal xanthate complexes. In all reported instances, the complexes are 1D chains, with 4,4'-bipyridine giving four different 1D chains with the metals Ni [77,80,81] and Cd [90], with different xanthate ligands. Two of the Ni complexes [80,81] and the Cd [90] complex exhibit an octahedral coordination environment, whereby two $\text{S,S}'$ chelating xanthate ligands and a 4,4'-bipyridine ligand make up the *trans*- N_2S_4 donor set (Fig. 17). In

these two examples bulkier xanthate ligands (isopropyl and butyl) were used, whereas when the smaller ethyl xanthate ligand is reacted with 4,4'-bipyridine and Ni [77] a zigzag chain is produced, where the 4,4'-bipyridine no longer occupies the *trans* positions, but instead adopts a *cis* confirmation with the two chelating xanthate ligands (Fig. 18).

The slightly less rigid ligand 1,2-bis(4-pyridyl)ethylene also adopts the *cis* confirmation when reacted with both Zn [83] and Ni [79]. The Ni complex, $[\text{Ni}((\text{S}_2\text{COCH}(\text{CH}_3)_2)_2(\text{C}_{12}\text{H}_{12}\text{N}_2))]$, as reported by Hill and Tiekink [79], has two chelating xanthate ligands and two *cis* bridging 1,2-bis(4-pyridyl)ethylene ligands coordinating to each metal centre, resulting in a zigzag 1D chain. Similar zigzag chains are observed when 1,2-bis(4-pyridyl)ethylene is reacted with Zn and the ethyl and butyl xanthate ligands [83]. The zigzag chains again result from a *cis* arrangement about the metal centre, however in these complexes the xanthate ligands do not chelate, but coordinate in a monodentate fashion, leaving the metal centre four-coordinate. Straight chain polymers

with *trans*-N₂S₄ coordination geometries were once again observed with the smaller bridging ligand pyrazine, with both Zn [84] and Ni [78].

5. Conclusions and outlook

Coordination polymers and sulphur-based metal complexes are both important classes of materials due to their ability to produce materials for applications such as gas storage, catalysis, magnetism, conductivity, nonlinear optical responses, catalysis, and ion exchange. Despite both being heavily explored independently, very little has been achieved, comparatively, from their overlap. Herein we have shown that various dtc, dithiocarboxylate and xanthate polymeric complexes can be prepared with a variety of metals, with the overwhelming majority arising from inclusion of additional bridging ligands, whether they are small counter ions or large rigid bidentate ligands. Each of the three classes of dithiolate ligands display the variety of coordination modes that are possible when bonded to metal centres, with combinations of two or more modes resulting in interesting polymeric structures. A range of halide bridged Ni and Pt dithiocarboxylate complexes as well as a few Cu dtc complexes showed that semiconducting properties can be carried across into polymeric complexes with these ligand systems.

There were, however, a few examples where bidentate and tridentate ligands were investigated. A tridentate dtc based ligand gave rise to macrocyclic arrays which extended with inclusion of supramolecular interactions, while a bidentate dithiocarboxylate ligand analogous to the highly explored oxygen based terephthalate produced a more rigid 1D chain. There is great potential to expand these promising outcomes through careful design and exploration of more bi-, tri- and tetradentate sulphur-based ligands.

Overall, however, sulphur-based CPs are a relatively underexplored class of compounds, but one which shows promise in terms of both structural interest and potential future applications.

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