Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2025, **54**, 11464

Addressing misconceptions in dithiocarbamate chemistry

David Pugh and Graeme Hogarth *

Received 8th May 2025,
Accepted 19th June 2025

DOI: 10.1039/d5dt01085c

rsc.li/dalton

Dithiocarbamates are monoanionic chelating ligands, easily prepared from CS_2 and secondary or primary amines, that find widespread use in agriculture, medicine, materials science and coordination chemistry. This is (in part) due to their ability to stabilise metals in a wide range of oxidation states, a result of *soft* (dithiocarbamate) and *hard* (thioureide) resonance forms. However, in the many thousands of publications on dithiocarbamate chemistry, some common misconceptions have arisen, often being accepted as truth. In this perspective we address some of these in the hope that, moving forward, the wider community will better grasp the nuances of the chemistry of this important ligand type.

1. Introduction

Dithiocarbamates, their complexes, and oxidised counterparts the thiuram disulfides (Fig. 1) find widespread uses in a diverse range of areas including: agriculture,[1,2] analytical chemistry,[3–7] coordination chemistry,[8–18] environmental remediation,[19–23] medicine,[24–29] enzyme inhibition,[30–36] medical imaging,[37–39] living polymerisation,[40–43] materials science[44–48] and as precursors to metal-sulfide nanomaterials.[49–52] They are a subset of the widely studied 1,1′-dithiolate ligands and close relatives of thiocarbamates and carbamates.[8,9] Despite being known for at least 150 years they remain an area of significant research activity. For example, with the recent identification of a new cell death mechanism termed cuprotosis,[53] the anti-cancer activity of $[Cu(S_2CNEt_2)_2]$, which has been known for over 40 years,[54–59] has once again come under the spotlight.[60–64] Thus, tetraethyl thiuram disulfide (Et_4TDS), better known as Disulfiram (Antabuse), is a drug that finds widespread use in the treatment of alcoholism.[65] It is rapidly metabolised in the gut (it is normally given orally) or in blood[66] to give diethyldithiocarbamate, which in turn can bind to Cu(II) to afford $[Cu(S_2CNEt_2)_2]$ *in situ*.

Dithiocarbamates are easily prepared, generally in high yields, upon reaction of CS_2 with secondary or primary amines generally in the presence of an added base.[8] Water is often used as the solvent, although reactions also proceed in MeOH and some other organic solvents. Reactions can be carried out in air, making dithiocarbamates easily accessible in less sophisticated lab environments. Consequently, this has led to an extremely large volume of research output: a search for "dithiocarbamate" in SciFinder© giving almost 25 000 hits and for "dithiocarbamato" another *ca.* 1500. Many of these publications are of excellent quality, some being cited thousands of times. However others contain errors and misconceptions, some of which are repeated so frequently as to be erroneously accepted as truth.

As researchers who are active in the area[67–72] and have written significant reviews,[8,24,49] we have read and closely scrutinised a considerable number of papers on dithiocarbamate chemistry. In doing so we have seen some errors-misconceptions being regularly repeated. In this contribution we address these, with the hope that they may appear less frequently in the future. In general, our intention is not to highlight individual contributions where errors have been made or perpetuated, however at times this is unavoidable. We accept that the majority are made in good faith and hope to avoid demonising individuals.

2. Synthesis of dithiocarbamates

(i) Amines are deprotonated by base, and it is the amide that undergoes nucleophilic attack at CS_2 to afford the dithiocarbamate

Primary and secondary amines are extremely basic, having pK_bs of *ca.* 4. Consequently, they are not acidic and have pK_as of *ca.* 40. Thus, upon dissolution in water (or an organic solvent), even following the addition of a strong base such as NaOH, they are not deprotonated. They are, however, nucleophilic and like many N-based nucleophiles can react directly with the electrophilic carbon in CS_2.[73] This generates a zwitterion which cannot be isolated or spectroscopically identified, presumably since the equilibrium lies to the left-hand side. It can, however, be deprotonated by the added base, which if it is

Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London SE1 1DB, UK. E-mail: graeme.hogarth@kcl.ac.uk

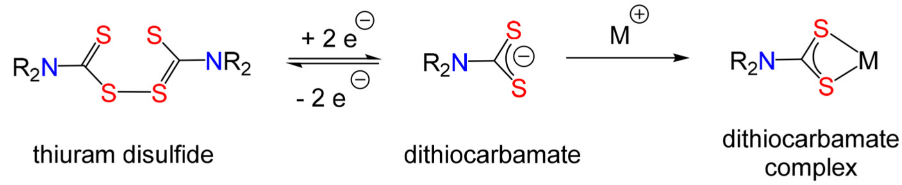

Fig. 1 Dithiocarbamates, their complexes and thiuram disulfides.

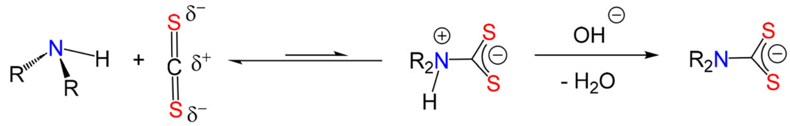

Fig. 2 Reaction of secondary amine with CS_2 in the presence of MOH as a base.

a hydroxide then simply affords water and the desired dithiocarbamate (Fig. 2).

Unfortunately, there are many examples in the literature that show the secondary (or primary) amine being deprotonated by the base and then suggesting that it is the generated amide $[NR_2]^-$ or $[NHR]^-$ that reacts with CS_2. As stated above, most bases used in the formation of dithiocarbamates are not basic enough to deprotonate the amine, and even if they were, the generated amides are very susceptible to hydrolysis and would immediately regenerate the amine. We note that alkali metal amides such as $LiNMe_2$ are highly pyrophoric and should be handled in a rigorously anhydrous environment (also see section 2-iii).

(ii) In the absence of an added base, CS_2 reacts with a primary or secondary amine to afford the dithiocarbamic acid

Many secondary and primary amines react directly with CS_2 and do not require added base. Thus, it is tempting to suggest that the reaction furnishes the free dithiocarbamic acid. This is, however, erroneous and rather this reaction generates the corresponding ammonium salt of the dithiocarbamate (Fig. 3).

Thus, it can be viewed in the same way as that above (Fig. 2), with the zwitterion being deprotonated by the amine which acts as both nucleophile and base. Thus, the overall stoichiometry is not 1 : 1 but rather 2 : 1, amine to CS_2.[74–76] Indeed, three purported crystal structures of dithiocarbamic acids have been reported[77–79] (one later revised).[80] The crystal structure of an adduct of hexylamine ($HexNH_2$) and the dithiocarbamic acid, $HexNHCS_2H$[78] is really the ammonium salt (Fig. 4a), but the proton has been incorrectly located on sulfur rather than hexylamine. Likewise, in the proposed amino acid derivative (Fig. 4b) the proton is actually located on the basic nitrogen.[79]

Sometimes, even when a second base has been added, the ammonium dithiocarbamate is (in part) generated in the reaction especially when the amine is a strong base, as the two compete to deprotonate the zwitterion. This is the case in the reaction of $^iBu_2NH$ and CS_2 in water with added NaOH, a reaction we have carried out numerous times in our lab. Thus, the off-white ammonium salt has poor water solubility and can precipitate, often being observed as a "scum" in the reaction vessel. Simply stirring in a warm (*ca.* 50–60 °C) water bath for 20–30 min leads to complete dissolution and formation of a clear pale-yellow solution of $NaS_2CNBu^i{}_2$.

Nice illustrations of an amine acting as both a base and a nucleophile are in the reaction of diamines with CS_2. For example, reaction of piperazine with CS_2 affords as the major product a zwitterionic product (Fig. 5) together with a small amount (*ca.* 5–10%) of the (so-called) double salt, thus providing an elegant method of desymmetrising a cheap diamine which can then be used to build up novel multimetallic arrays.[81–86]

(iii) Reactions of diarylamines with CS_2 in the presence of MOH afford diaryldithiocarbamates

Anilines are nucleophilic enough to react directly with CS_2 and thus dithiocarbamates, $[ArNHCS_2]^-$ are readily available.[87] In contrast, diphenylamine and other diarylamines are not nucleophilic enough and will not react directly with CS_2 in the presence of standard bases. Thus, to prepare $[Ar_2NCS_2]^-$, the corresponding amides $[NAr_2]^-$ need to be accessed; these are nucleophilic enough to react with CS_2. Reagents that are basic

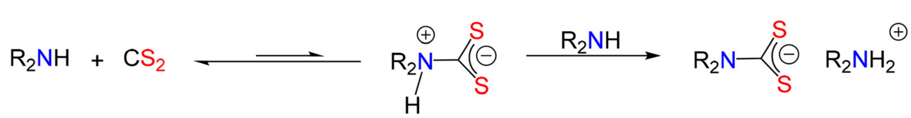

Fig. 3 Reaction of secondary amine with CS_2 in the absence of a second base.

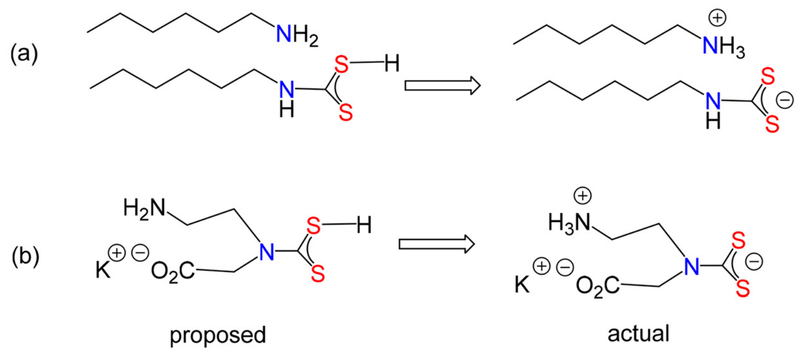

Fig. 4 Actual and proposed forms of crystallographically characterised "dithiocarbamic acids".

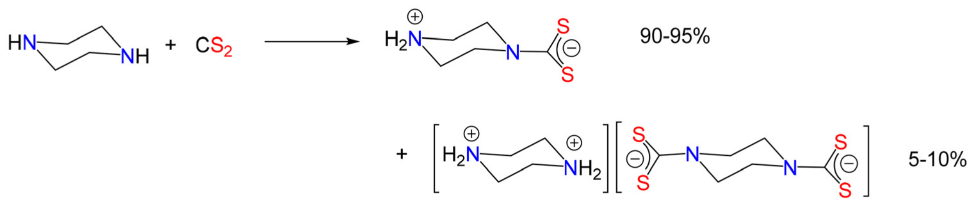

Fig. 5 Reaction of piperazine with CS_2.

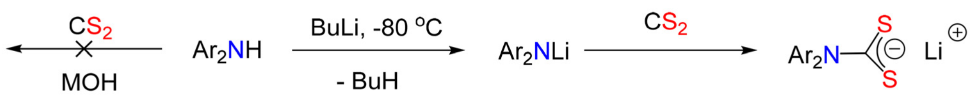

Fig. 6 Generation of diaryldithiocarbamate salts upon addition of CS_2 to $LiNAr_2$.

enough to deprotonate Ar_2NH include ^nBuLi,[88,89] $NaBH_4$,[90] sodium amide[91,92] and $KOBu^t$.[67] All require water-free conditions otherwise the neutral amines will simply be regenerated. Thus, we have recently developed a preparation[88] that uses ^nBuLi in thf to afford $LiNAr_2$ at low temperatures, which in turn react with CS_2 to form LiS_2CNAr_2 in (essentially) quantitative yields[67] (Fig. 6). Once formed these dithiocarbamate salts are very stable and can be stored indefinitely as solids in air. We have also had success with using $KOBu^t$ in thf but found this not to be reproducible in regular lab grade solvents. As stated above, other authors have used $NaBH_4$ but in our hands this was not successful.

(iv) Amides such as phthalimide and succinimide react with CS_2 to generate dithiocarbamates

As discussed above, amines need to be relatively nucleophilic if a dithiocarbamate is to be made directly, and amides are not nucleophilic enough to react directly with CS_2. Despite this, several publications claim the synthesis of amide-derived dithiocarbamates and their complexes,[93–97] some of which we have failed to reproduce.[93,94] As highlighted for diarylamines, a second approach is to initially deprotonate to yield the more nucleophilic anion. In this way, we have tried reacting commercially available sodium phthalimide with CS_2 under a variety of conditions but in all instances, we found no evidence for the formation of the corresponding dithiocarbamate (Fig. 7).

In contrast, 2-pyrrolidone does react with CS_2 in the presence of bases such as KOH, to afford a dithiocarbamate which can be quenched with electrophiles to give the corresponding ester.[98–100] Formamide also reacts with CS_2 in the presence of base as confirmed by the crystal structure of $KS_2CNH(CHO)$.[101] There is a short paper on metal complexes of 2-pyrrolidone dithiocarbamate,[102] which suggests this ligand type could be further developed, along with that of iso-indolinone, for which the dithiocarbamate has not been reported but is likely accessible.

There are several authenticated examples of amide-functionalised dithiocarbamate complexes, being accessible *via*

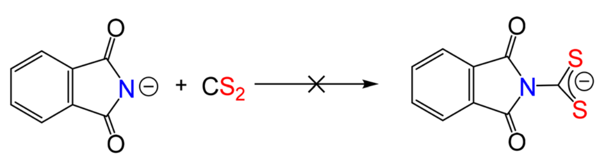

Fig. 7 Unsuccessful reaction of phthalimide with CS_2.

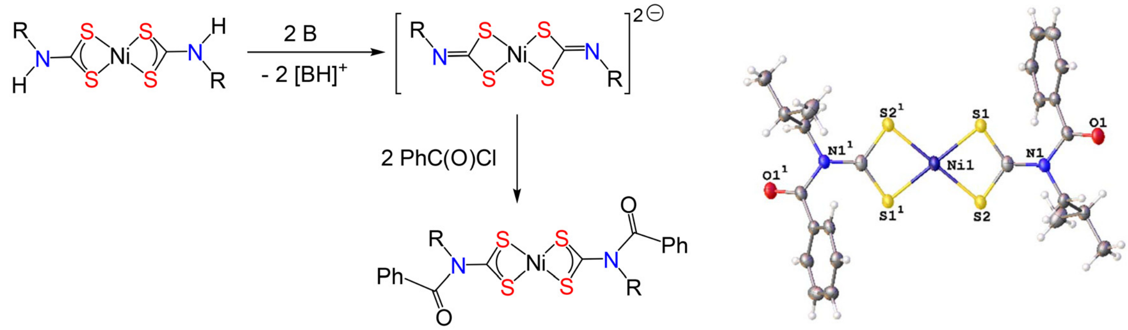

Fig. 8 Synthesis and molecular structure (R = ^{i}Bu) of amide-functionalised nickel bis(dithiocarbamate) complex.

dithiocarbimate complexes.[103] For example, deprotonation of the corresponding primary amine-derived nickel complexes, $[Ni(S_2CNHR)_2]$, followed by quenching with electrophiles such as acetic anhydride and benzoyl chloride (Fig. 8).[104–107] These amide-dithiocarbamate complexes are very stable and show interesting physical properties, something we have recently been reinvestigating in our own research.[107]

3. Stability of dithiocarbamates and thiuram disulfides

(i) Dithiocarbamic acids are stable and isolable entities

A major misconception in dithiocarbamate chemistry, being especially prevalent in the biological domain, is that dithiocarbamic acids are stable entities. Thus, as has been well studied, disulfiram is rapidly reduced *in vivo* to give two equivalents of diethyldithiocarbamate, which is often erroneously written as the free acid.[108] Chemists are also not immune to this mistake and often (as noted above) the direct reaction of an amine with CS_2 is purported to give the dithiocarbamic acid rather than the ammonium salt of the dithiocarbamate.[77–79,109–112] Dithiocarbamates are basic, especially those with two alkyl substituents, and at pH 7 or below (indeed even above this in some cases) they are protonated to give the dithiocarbamic acids. However, these are unstable and, in most cases, decompose rapidly to give CS_2 and the corresponding ammonium salt (Fig. 9). Many publications have addressed the decomposition process, and mechanistic aspects have been elucidated.[113–124] Here is not the place to go into detail but the main decomposition route involves a hydrogen-bonded intermediate, rather than zwitterion formation resulting from proton transfer from sulfur to nitrogen. Decomposition is accelerated upon lowering the pH and this is why dithiocarbamates are generated under basic conditions. Recently, the generation and decomposition of dithiocarbamic acids has been repurposed as a route for the release of CS_2.[125] These studies show that their lifetimes are highly dependent upon the nature of the substituents, those with two aryl groups being stable for up to 24 h at pH 7.4.[125] Dithiocarbamic acids of primary amines are especially unstable[119] but still appear in the literature.[126] Dithiocarbamates of primary amines are widely used as precursors for the generation of organic isothiocyanates[127,128] and other sulfur-containing organics.[129,130]

(ii) Dithiocarbamate halides are accessible

A relatively uncommon misconception, but one that is increasingly appearing in the literature, is the idea that halides of dithiocarbamates, especially the iodide, are accessible.[131] It is well known that iodine acts as an oxidising agent, converting dithiocarbamates into thiuram disulfides, rather than forming the corresponding iodide (Fig. 10). With primary amine dithiocarbamates this (likely) generates the unstable thiuram disulfide (see below), and not the iodide.[132,133]

It is worth adding that, while not a misconception, the redox chemistry of the dithiocarbamate ligand is often overlooked, which can lead to an over-simplification of discussion of redox events when coordinated to metal centres. Examples are reactions of $[M(S_2CNR_2)_2]$ (M = Zn, Cd) with I_2.[134,135] Thus, reduction of iodine is rapid at the non-redox active Zn(II) centre as it is the dithiocarbamate that is oxidised, on metal, to form the corresponding thiuram disulfide complexes (Fig. 11).

(iii) Thiuram disulfides of primary amines are stable

Thiuram disulfides generated from secondary amines are generally very stable and can be easily isolated, purified and stored. Indeed, they are often easier to store than the corresponding dithiocarbamates and can then be reduced *in situ* to

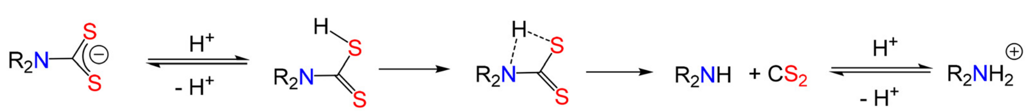

Fig. 9 *In situ* generation and decomposition of dithiocarbamic acids.

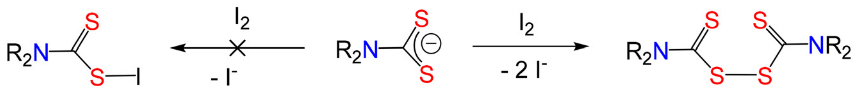

Fig. 10 I_2 oxidation of dithiocarbamate to thiuram disulfide.

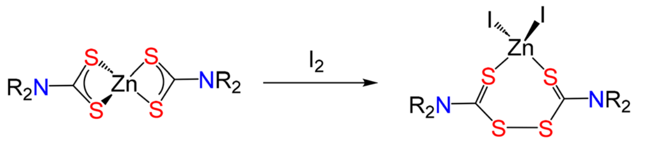

Fig. 11 I_2 addition to $[Zn(S_2CNR_2)_2]$ and formation of a thiuram disulfide complex.

provide a source of dithiocarbamate. In contrast, oxidation of primary amine dithiocarbamates affords thiuram disulfides with poor stability, decomposing to afford isothiocyanates and/or thioureas, depending upon the reaction conditions used[127,136–140] (Fig. 12).

4. Accessibility and air-stability of $[M(S_2CNR_2)_2]$

One of the beauties of doing transition metal dithiocarbamate chemistry is their ease of synthesis, isolation, and purification, much of which can be carried out in air. Thus, complexes normally have moderate to good solubility in polar organic solvents, and many can be crystallised in air, either by slow evaporation or the (careful) addition of an anti-solvent such as hexane or petroleum ether. In this way, the crystal structures of thousands of dithiocarbamate complexes have found their way into the Cambridge Crystallographic Data Centre (CCDC).[141] However, not all dithiocarbamate complexes are air stable. For example, while bis(dithiocarbamate) complexes, $[M(S_2CNR_2)_2]$ (M = Ni, Cu, Zn) are air and moisture stable, in contrast those of the other first row transition elements can only be prepared (if at all) under rigorously oxygen-free conditions.[142–144] Thus, generally, if they can be prepared, $[M(S_2CNR_2)_2]$ complexes are readily oxidised in air, with M(III) complexes being favoured. Below we discuss each metal type individually as their chemistry differs. We also describe some related chemistry (where appropriate) to provide context.

(i) M = Ti, V, Cr

The chemistry of titanium is dominated by the +4 and +3 oxidation states, and dithiocarbamates are no exception. A Ti(II) complex has briefly been mentioned in the literature,[145] reaction of $[Ti(NEt_2)_3]$ and CS_2 being reported to give a mixture of $[Ti(S_2CNEt_2)_2]$ and $[Ti(S_2CNEt_2)_4]$. However, no characterising data or reaction details were given. The existence and stability of red Ti(IV) complexes $[Ti(S_2CNR_2)_4]$ are without doubt, being prepared upon insertion of CS_2 into $[Ti(NR_2)_4]$,[146] or upon addition of LiS_2CNR_2 to $TiBr_4$.[147] Both $[Ti(S_2CNEt_2)_4]$[148] and $[Ti(S_2CNPr^i{}_2)_4]$[147] have been crystallographically characterised. One report suggests that reaction of NaS_2CNR_2 with $TiCl_3$ in EtOH affords $[Ti(S_2CNR_2)_3]$ as brown- or yellow-green solids,[149] but there are no later mentions of this type of complex in the literature. Thus, the stability of $[Ti(S_2CNR_2)_3]$, their potential disproportionation to $[Ti(S_2CNR_2)_2]$ and $[Ti(S_2CNR_2)_4]$, and structure and stability of the former remain issues that require clarification. Interestingly, it has recently been established that dithiocarbamates can coordinate to Ti(0), thus, oxidation of $[Ti(CO)_6]^{2-}$ by thiuram disulfides affords $[Ti(CO)_4(S_2CNR_2)]^-$ which adopt an unexpected trigonal prismatic geometry.[150] There may yet be new things to discover in titanium dithiocarbamate chemistry.

The only V(II) dithiocarbamate complex reported is light brown $[V(S_2CNEt_2)_2]$, formed under rigorously oxygen-free conditions upon addition of two equivalents of NaS_2CNEt_2 to VCl_2 in MeCN in a dry box.[143] Unfortunately, no characterising data was given, but it was reported to be soluble in warm 1,2-dichlorobenzene, so may be worthy of reinvestigation. In air, addition of $[R_2NH_2][S_2CNR_2]$ to $VBr_2{\cdot}6H_2O$ affords $[V(S_2CNR_2)_3]$.[151] The diethyl derivative has been crystallographically characterised[152] and magnetic measurements show a S = 1 ground state with two unpaired electrons.[153] Possibly, $[V(S_2CNR_2)_2]$ are fleetingly formed but readily oxidised, and putative $[V(S_2CNR_2)_2]^+$ reacts with further dithiocarbamate. The reduction chemistry of $[V(S_2CNEt_2)_3]$ has been investigated and reveals a reversible one-electron process.[154] Eight-coordinate V(IV) complexes, $[V(S_2CNR_2)_4]$, are accessible from the insertion of CS_2 into $[V(NR_2)_4]$,[155] but upon heating they undergo intramolecular electron transfer resulting in elimination of thiuram disulfide and formation of $[V(S_2CNR_2)_3]$. Formal oxidation products of $[V(S_2CNR)_2]$, namely vanadyl complexes $[VO(S_2CNR_2)_2]$, are easily prepared[156] and have been extensively investigated as potential insulin mimetics[157] and molecular qubits.[158] Thus, akin to the titanium chemistry, even the

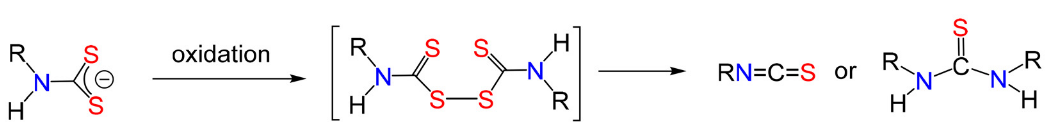

Fig. 12 Formation and decomposition of primary amine thiuram disulfides.

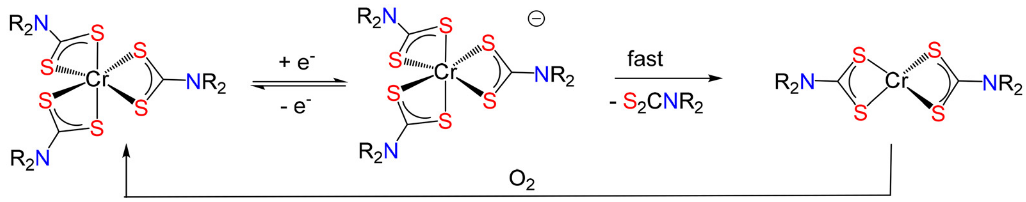

Fig. 13 Formation of $[Cr(S_2CNR_2)_2]$ *via* reduction of $[Cr(S_2CNR_2)_3]$ and back oxidation.

simple dithiocarbamate chemistry of vanadium requires further investigation.

Chromium bis(dithiocarbamate) complexes are indisputably accessible, but extremely air sensitive, so unless rigorous experimental methods are utilised it is the analogous d^3 Cr(III) complexes, $[Cr(S_2CNR_2)_3]$ that are isolated.[159–161] The first synthesis of $[Cr(S_2CNEt_2)_2]$ was reported by Fackler and Holah in 1966,[162] being described as a pyrophoric yellow-green solid. It has subsequently been prepared from thermolysis of $[Cr(CO)_6]$ and $[Hg(S_2CNEt_2)_2]$.[163] In solution $[Cr(S_2CNEt_2)_2]$ is extremely sensitive to air oxidation, converting rapidly to blue $[Cr(S_2CNEt_2)_3]$. Very few derivatives have been prepared and there are no crystal structure determinations, thus molecular structure(s) of $[Cr(S_2CNR_2)_2]$ remain unknown, although most likely they are polymeric in the solid state, and tetrahedral in the gas phase or solution. Electrochemical studies of $[Cr(S_2CNR_2)_3]$ show that they undergo a one-electron reduction, with the generated $[Cr(S_2CNR_2)_3]^-$ rapidly losing a dithiocarbamate to give $[Cr(S_2CNR_2)_2]$[164] (Fig. 13). However, all attempts to isolate or characterise $[Cr(S_2CNR_2)_2]$ generated in this way have led only to rapid back oxidation and regeneration of $[Cr(S_2CNR_2)_3]$, again highlighting their extreme air-sensitivity.

Non-homoleptic Cr(II) dithiocarbamate complexes can be prepared. For example, room temperature addition of $[CpCr(CO)_3]_2$ and tetraethyl thiuram disulfide affords $[CpCr(CO)_2(S_2CNEt_2)]$ in good yields.[165]

(ii) M = Mo, W

We briefly consider the heavier group 6 homologues, $[Mo(S_2CNR_2)_2]$ and $[W(S_2CNR_2)_2]$. The synthesis and X-ray crystal structure of $[Mo(S_2CNEt_2)_2]$ has been claimed[166] but is erroneous: the structure presented is that of $[Ni(S_2CNEt_2)_2]$ with a misassigned metal atom.[167] Complexes of the stoichiometry Mo : dithiocarbamate 1 : 2 are known. Thus, reactions of $[Mo_2(\mu\text{-}OAc)_4]$ with four equivalents of dithiocarbamate afford $[Mo_2(\mu\text{-}S_2CNR_2)_4]$ as green solids.[168] However, the latter are thermally unstable and upon heating undergo C–S bond scission to yield Mo(V) thiocarboxamide complexes, $[Mo(\mu\text{-}S)(S_2CNR_2)(SCNR_2)]_2$ as shown crystallographically (R = ^{i}Pr).[169] Related W(II) complexes, $[W(S_2CNR_2)_2]$, remain unreported, but both *cis*-$[W(CO)_2(S_2CNR_2)_2]$ and $[W(CO)_3(S_2CNR_2)_2]$ are known[170] as are the corresponding Mo(II) carbonyl complexes.[171]

(iii) $[Mn(S_2CNR_2)_2]$

Bright yellow $[Mn(S_2CNR_2)_2]$ complexes can easily be prepared, but both the reaction and work-up must be carried out under rigorously inert conditions.[172,173] The molecular structure of only one example, namely $[Mn(S_2CNEt_2)_2]$, has been reported (Fig. 14).[174] It is a coordination polymer containing octahedral Mn(II) centres resulting from the dithiocarbamates binding in a bridging manner.

Many papers detail reactions of two equivalents of dithiocarbamates with Mn(II) salts that have been carried out in water and air, and invariably the generated products are dark (often violet-purple) paramagnetic solids formulated as $[Mn(S_2CNR_2)_2]$. Authors often cite elemental analysis data as proof of this formulation. Indeed, fits with calculated values are often good, albeit in many cases a small amount of bound water (between 0.5 and 2 molecules) are suggested. Recently, this issue has been addressed, and it is now unequivocally established that the dark product described is a Mn(III) oxygen adduct.[175] The precise nature of this adduct is less clear, with the authors suggesting it is monomeric, but a recent crystal structure (Fig. 15) has shown that (at least in part) it is a dimeric oxygen-bridged complex.[176]

The colour of the oxygen adducts is very similar to that for Mn(III) complexes, $[Mn(S_2CNR_2)_3]$, generated upon addition of three equivalents of dithiocarbamate to Mn(II) salts in air, as is the spectroscopic data. Thus, it is not easy to differentiate between the two. If two equivalents of dithiocarbamate are

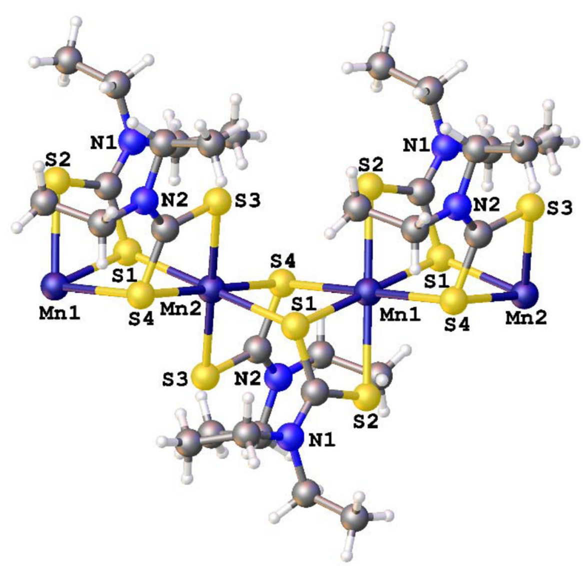

Fig. 14 Part of the polymeric structure of $[Mn(S_2CNEt_2)_2]$.[174]

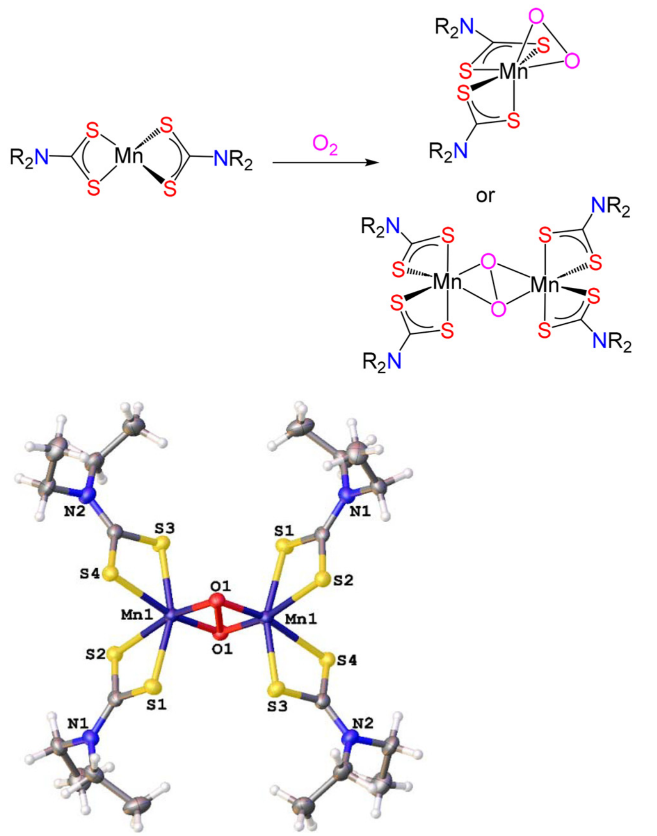

Fig. 15 Oxidation of [Mn(S_2CNR_2)$_2$] with proposed Mn(III) adducts and the molecular structure of [Mn_2(S_2CNEt_2)$_4$(μ-O_2)].[175,176]

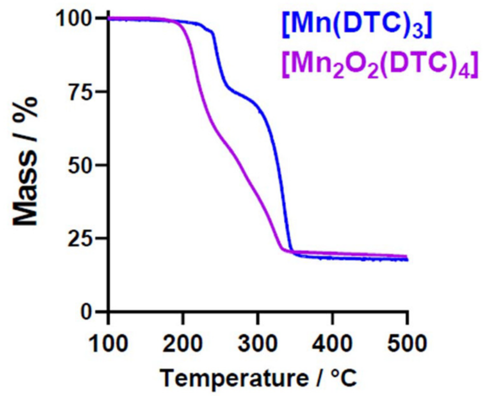

Fig. 16 TGA data for [Mn(S_2CNEt_2)$_3$] and [Mn_2(S_2CNEt_2)$_4$(μ-O_2)].[176]

added to Mn(II) salts in water under argon then heavy yellow precipitates result, which are unequivocally [Mn(S_2CNR_2)$_2$]. Further, later exposure to oxygen (bubbling through solution works best to ensure full oxidation) reliably affords the pure oxygen adduct.[175] Addition of more dithiocarbamate salt to the latter gives [Mn(S_2CNR_2)$_3$], although it is hard to know exactly when the reaction is complete and to ensure that it is, a slight excess of dithiocarbamate is recommended.[175]

Manganese dithiocarbamate complexes are becoming widely used as single source precursors (SSPs) to manganese sulfide nanomaterials.[177–180] In this respect, the accidental use of the oxygen adduct may be advantageous. Thus, oxygen adducts have a higher manganese content than [Mn(S_2CNR_2)$_3$] and, as shown by thermogravimetric analysis (TGA) for the diethyl derivatives (Fig. 16), decompose at lower temperatures. Indeed, TGA is a good way of differentiating between these two Mn(III) dithiocarbamate complexes.[176] Finally, we note that [Mn(S_2CNR_2)$_3$] decomposes in a two-step process, the former being associated with loss of a dithiocarbamate and *in situ* formation of [Mn(S_2CNR_2)$_2$], thus negating the need to isolate air sensitive Mn(II) complexes.

An early application of dithiocarbamates was as fungicides, with manganese containing Maneb© being widely used. It is formed from the reaction of Mn(II) salts with Nabam©, the bis(dithiocarbamate) generated from ethylene diamine (Fig. 17). More recently it has been linked to the development of Parkinson's disease[181,182] and since 2009 has been banned in the European Union, a fate also experienced by the zinc complex, Zineb©, which was also previously used as a pesticide.

Maneb© and Zineb© were used in agriculture for many years and are proposed to have polymeric structures, as has the double hydration product of Maneb© namely [Mn($S_2CNHC_2H_4NHCS_2$)·2H_2O]$_n$. Recently a good quality molecular structure of the dimethylformamide (dmf) adduct [Mn($S_2CNHC_2H_4NHCS_2$)·2dmf]$_n$ was reported[183] (Fig. 18) and confirms this. Manganese is in the +2 oxidation state but, importantly, has an octahedral coordination geometry with coordination of two *cis* dmf molecules (there are another two non-coordinated dmfs not shown). Likely hydrated Maneb© has a very similar structure except with bound water. Another interesting observation is that while pure samples of this adduct and Maneb© are yellow, the latter ages over time, becoming dark.

(iv) [Fe(S_2CNR_2)$_2$]

Like their manganese counterparts, [Fe(S_2CNR_2)$_2$] can be prepared and isolated but are extremely air sensitive and should be handled in a dry box or a high quality Schlenk line environment. When prepared under the correct conditions they are described as chocolate brown,[162] pink[142] or red[184] solids. Crystal structures of two polymorphs of [Fe(S_2CNEt_2)$_2$][185,186] show that it adopts a dimeric structure in the solid state (Fig. 19). Each iron centre is 5-coordinate, being best described as a distorted trigonal bipyramid. No other molecular structures have been determined, but there is some early evidence from Mössbauer studies that some derivatives may be coordination polymers.[187,188]

As with the manganese chemistry described above, many authors describe the purported synthesis of Fe(II) bis(dithiocarbamate) complexes in air, and thus their assignment is clearly wrong. Unlike the manganese chemistry, however, it is less clear exactly what they have made if only two equivalents of dithiocarbamate are used. Thus, oxygen adducts of [Fe

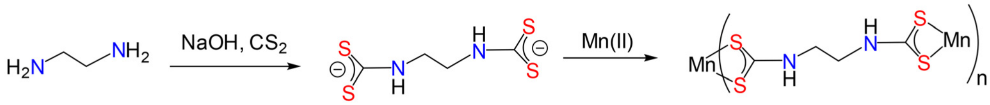

Fig. 17 Formation of Nabem© and reaction with Mn(II) salts to produce Maneb©.

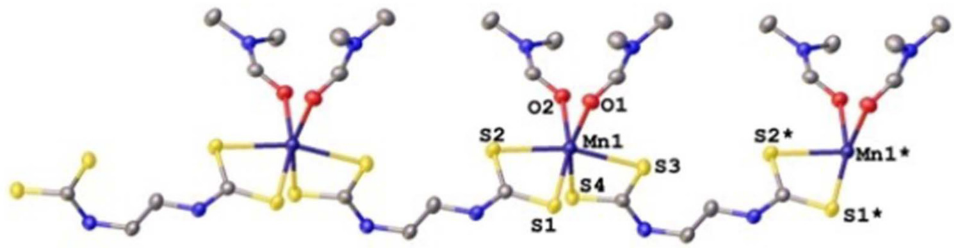

Fig. 18 Part of the polymeric structure of $[Mn(S_2CNHC_2H_4NCS_2)\cdot 2dmf]_n$.[183]

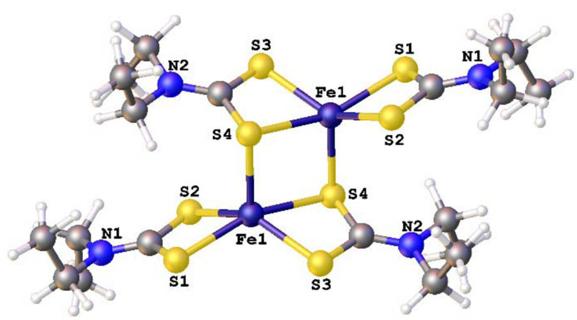

Fig. 19 The molecular structure of $[Fe(S_2CNEt_2)_2]_2$.[185]

$(S_2CNR_2)_2]$ have not been reported. These complexes do undergo rapid addition, for example addition of bis(perfluoromethyl)-1,2-dithietene affords Fe(III) complexes (Fig. 20) showing how prone they are to oxidation.[189] It is also known that $[Fe(S_2CNR_2)_2]$ react with excess dithiocarbamate to afford yellow $[Fe(S_2CNR_2)_3]^-$, which are also extremely air sensitive, being rapidly oxidised to brown Fe(III), $[Fe(S_2CNR_2)_3]$.[190] Thus, it is most likely that reaction of two equivalents of dithiocarbamate with Fe(II) salts in air simply gives reduced yields of $[Fe(S_2CNR_2)_3]$ along with some unreacted Fe(II) salt.

Bis(dithiocarbamate) complexes $[Fe(S_2CNR_2)_2]$ also bind neutral donor ligands, as shown in crystal structures of a dmf adduct of the morpholine-dithiocarbamate complex (Fig. 21a)[191] and a DABCO adduct of $[Fe(S_2CNEt_2)_2]$ which co-crystallises with C_{60}[144] (Fig. 21b). Thus, from aqueous solutions, it may be that a species $[Fe(S_2CNR_2)_2\cdot H_2O]$ precipitates out. Interestingly, an NMR spectrum of $[Fe(S_2CNC_4H_8O)_2\cdot dmf]$ run in $CDCl_3$ was found to be identical to that of paramagnetic $[Fe(S_2CNC_4H_8O)_3]$, suggesting oxidation and ligand arrangement upon dissolution in this weakly acidic solvent.[191] Thus, it might be that Fe(II) is reducing enough to convert H^+ into H_2 with concomitant formation of Fe(III).

The Fe(II) oxidation state can be also stabilised by binding of carbonyls in *cis*-$[Fe(CO)_2(S_2CNR_2)_2]$[192,193] and NO in $[Fe(NO)(S_2CNR_2)_2]$.[194,195] Indeed, the binding of NO to $[Fe(S_2CNEt_2)_2]$, as determined by the distinctive EPR spectrum of $[Fe(NO)(S_2CNEt_2)_2]$, is an accepted way of determining the presence of this important signalling gas.[196–198] It is noteworthy, however, that reaction of NO with $[Fe(S_2CNEt_2)_3]$ also affords $[Fe(NO)(S_2CNEt_2)_2]$ (together with thiuram disulfide as a byproduct).[198] Photolysis of $[Fe(S_2CNEt_2)_3]$ also results in elimination of thiuram disulfide and formation of $[Fe(S_2CNEt_2)_2]$, which can be trapped with bis(diphenylphosphino)ethane (dppe) to afford $[Fe(\kappa^2\text{-dppe})(S_2CNEt_2)_2]$.[199] This suggests that there is a fine redox balance between the reducible Fe(III) centre and the oxidisable dithiocarbamate. Indeed, we have found using *in situ* EXAFS, that upon warming $[Fe(S_2CN^iBu_2)_3]$ in oleylamine at 60 °C, reductive elimination of thiuram disulfide results with concomitant formation of the corresponding Fe(II) complex.[193] Further, TGA measurements show that *cis*-$[Fe(CO)_2(S_2CNR_2)_2]$ lose both carbonyls at relatively low temperatures to afford $[Fe(S_2CNR_2)_2]$. Thus, $[Fe(S_2CNR_2)_2]$, $[Fe(S_2CNR_2)_3]$ and *cis*-$[Fe(CO)_2(S_2CNR_2)_2]$ are all effectively equivalents when used as SSPs[193] thus negating the need to isolate air sensitive $[Fe(S_2CNR_2)_2]$.

Neither $[M(S_2CNR_2)_2]$ (M = Ru, Os) appear in the reliable literature, with both metals favouring the M(III) state $[M(S_2CNR_2)_3]$, but like iron, carbonyl-stabilised M(II) complexes *cis*-$[Ru(CO)_2(S_2CNR_2)_2]$[200] and *cis*-$[Os(CO)_2(S_2CNR_2)_2]$[201–203] are accessible.

(v) $[Co(S_2CNR_2)_2]$

The theme continues into the chemistry of cobalt. Like iron and manganese, cobalt forms stable M(III) tris(dithiocarbamate) complexes $[Co(S_2CNR_2)_3]$, the low spin d^6 electronic configuration allowing NMR characterisation.[204–206] In contrast, while the corresponding M(II) species $[Co(S_2CNR_2)_2]$ are accessible, they are extremely air-sensitive and paramagnetic, with $[Co(S_2CNEt_2)_2]$ being described as a dark green-brown solid.[142]

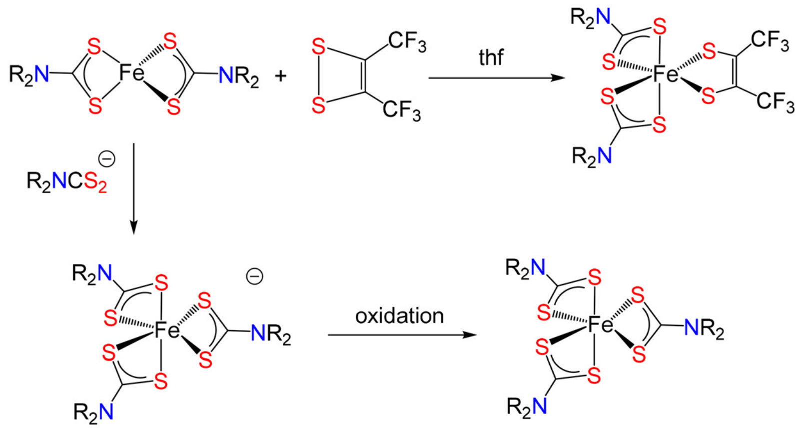

Fig. 20 Reactions of $[Fe(S_2CNR_2)_2]$ with a dithietane resulting in oxidation, and addition of further dithiocarbamate followed by oxidation.

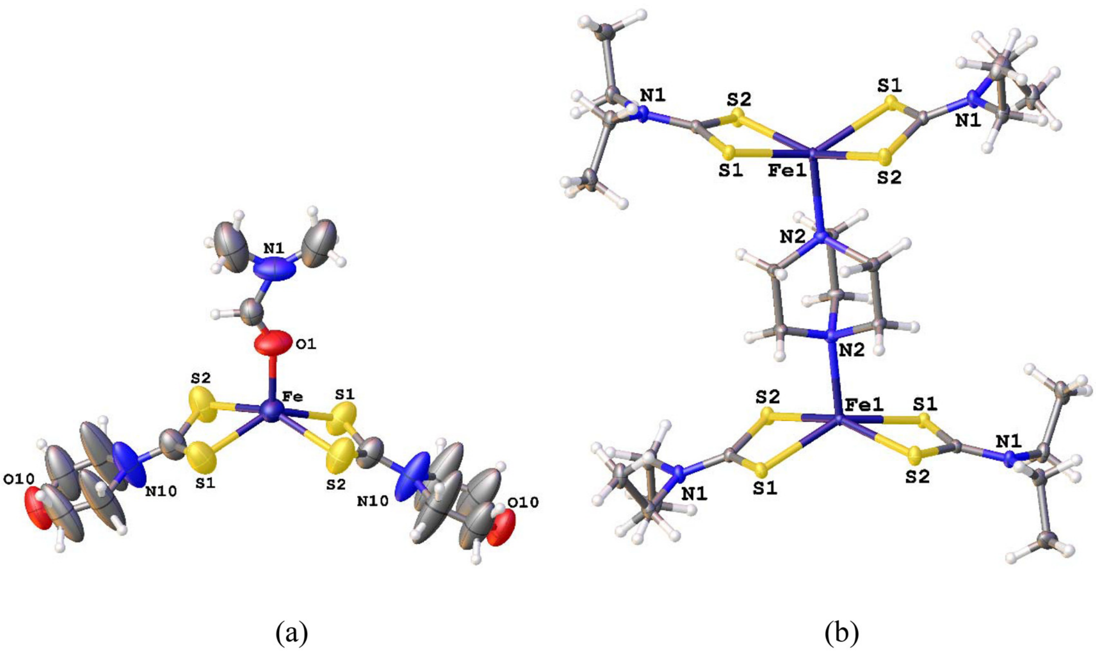

Fig. 21 Molecular structure of (a) $[Fe(S_2CNC_4H_8O)_2{\cdot}dmf]$[191] and (b) $[\{Fe(S_2CNEt_2)_2\}_2DABCO]$ as part of a large structure with $C_{60}{\cdot}2DABCO$.[144]

It is telling that there are no crystal structures of $[Co(S_2CNR_2)_2]$ and examples of authentic syntheses and characterisation are rare. Most authors report the formation of green precipitates from reactions of dithiocarbamate salts with $CoCl_2{\cdot}6H_2O$ in air, *i.e.* they actually generate $[Co(S_2CNR_2)_3]$. Recently, Khitrich and co-workers provided some evidence for the formation of $[Co(S_2CNR_2)_2]$,[207] suggesting that, provided pH is kept between 6–7, then even in air aqueous solutions of $[CoCl_2]$ react with two equivalents of NaS_2CNR_2 to afford $[Co(S_2CNR_2)_2]$ and note that in the solid state they are air stable. Good elemental analysis data are presented, and powder X-ray diffraction studies reveal (for those that are not amorphous) the absence of $[Co(S_2CNR_2)_3]$. Further, magnetic moments of 2.19–2.45 BM suggest that they have one unpaired electron, consistent with a square planar geometry. Interestingly, when dissolved in organic solvents they oxidise rapidly with formation of $[Co(S_2CNR_2)_3]$ and $[Co(OH)_2]$ (Fig. 22). Clearly more work in this area is warranted.

Electrochemical reduction of $[Co(S_2CNR_2)_3]$ leads to dithiocarbamate loss to give $[Co(S_2CNR_2)_2]$, but back oxidation is facile.[208] Chemical reduction of $[Co(S_2CNR_2)_3]$ by excess Zn/Hg in CH_2Cl_2 results in a slow (*ca.* 3 h) darkening of the green solution and when canulated under nitrogen onto PhI = NTs, the Co(II) complexes react *via* insertion into the Co–S bonds to afford crystallographically characterised $[Co\{TsNSC(NR_2)SNTs\}_2]$[209] (Fig. 23). Thus, it is chemically possible to prepare $[Co(S_2CNR_2)_2]$ in organic solvents but oxygen must be rigorously excluded.

We note that there are no authentic examples of $[Rh(S_2CNR_2)_2]$ or $[Ir(S_2CNR_2)_2]$ complexes,[210,211] all purported

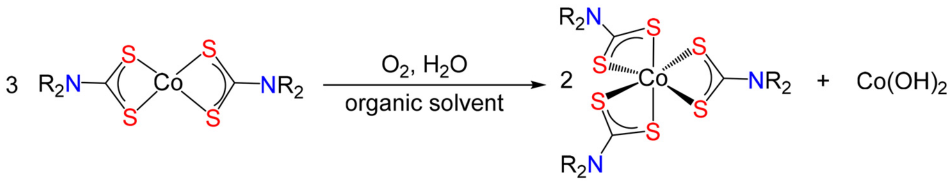

Fig. 22 Proposed decomposition of $[Co(S_2CNR_2)_2]$ in organic solvents.[207]

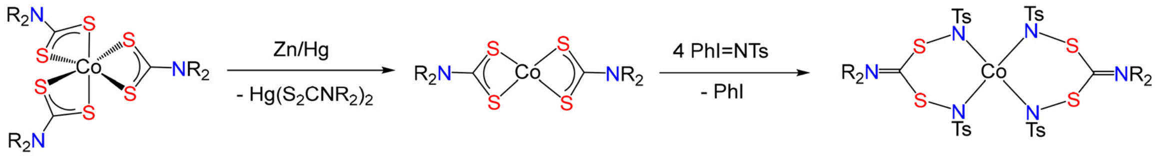

Fig. 23 Reductive generation of $[Co(S_2CNR_2)_2]$ and trapping *via* multiple NTs insertion in the Co–S bonds.

syntheses being likely that of the analogous $[M(S_2CNR_2)_3]$ complexes.[212,213] Electrochemical reduction of $[Rh(S_2CNR_2)_3]$ is irreversible and shown to be a two-electron process with formation of $[Rh(S_2CNR_2)_2]^-$ and dithiocarbamate being suggested.[214]

5. Structure and stability of dithiocarbamate complexes

(i) $[M(S_2CNR_2)_2]$ (M = Mn, Fe, Co) are all square planar

In solution or the gas phase, the molecular structures of group 10 bis(dithiocarbamate) complexes and $[Cu(S_2CNR_2)_2]$ are square planar. In the solid state, the 4-coordinate square planar arrangement is maintained for $[M(S_2CNR_2)_2]$ (M = Ni, Pd, Pt), but the precise metal coordination environment for copper varies with substituents due to secondary Cu⋯S interactions.[8,13] The solution and gas phase structures of $[M(S_2CNR_2)_2]$ (M = Mn, Fe, Co) remain unknown, although some authors suggest that all are square planar. This seems highly unlikely for $[Mn(S_2CNR_2)_2]$ as for a d^5 electronic conformation one would not expect the difference in crystal field stabilisation energies (CFSEs) between tetrahedral and square planar geometries to override steric effects, even when the preferred bite angle for dithiocarbamates is less than 90°. An early communication suggested that, in ethanol, $[Mn(S_2CNEt_2)_2]$ adopts a spin quartet state, *i.e.* has 3 unpaired electrons,[215] although it was later shown that this result was erroneous, as measurements had been made on a partially oxidised sample. Upon rigorous exclusion of air, magnetic measurements on $[Mn(S_2CNEt_2)_2]$ and other derivatives show that they adopt a ground state with 5 unpaired electrons.[172] Thus, it seems likely that $[Mn(S_2CNR_2)_2]$ have a distorted tetrahedral coordination geometry, although a recent DFT study suggests a square-planar arrangement, which may be a local minimum.[216] In a similar vein, iron complexes, $[Fe(S_2CNR_2)_2]$, with a d^6 electronic configuration have been shown to have 4 unpaired electrons,[186] being inconsistent with a square-planar array. Nevertheless, recent DFT calculations propose a local FeS_4 geometry with D_{2h} symmetry, consistent with a square planar geometry.[217] Clearly, accurate calculations are required to corroborate the actual coordination geometry. The absence of any crystallographic data makes it harder to predict the molecular geometry of d^7 $[Co(S_2CNR_2)_2]$, but they are likely square-planar, as supported by the magnetic susceptibility measurements and DFT calculations.[218]

(ii) Ru(III) complexes $[Ru(S_2CNR_2)_3]$ and $[Ru(S_2CNHR)_3]$ are diamagnetic

Iron tris(dialkylDTC) complexes, $[Fe(S_2CNR_2)_3]$, have been widely studied as spin crossover complexes as they can adopt either high spin (HS) $^6A_1$ or low spin (LS) $^2T_2$ electronic configurations, the position of the equilibrium being affected by the nature of the alkyl-substituents and external factors such as temperature and pressure.[219–222] Receiving less attention are analogous Ru(III) complexes, $[Ru(S_2CNR_2)_3]$, although a number of early papers established their fluxional distorted octahedral structures[223] and paramagnetic nature,[224,225] the latter being as expected for a d^5 electronic configuration. Nevertheless, several publications claim to have prepared diamagnetic Ru(III) tris(dithiocarbamate) complexes of both secondary and primary amines, characterised by (almost perfect) elemental analysis data and ^1H NMR peaks in the standard 0–10 ppm range.[226–228] Interestingly, ^1H NMR spectroscopy can be used to part-characterise $[Ru(S_2CNR_2)_3]$, although peaks are observed across a *ca.* 40 ppm range, as expected for a weak (low spin) paramagnetic system.[229–231] Diamagnetic complexes can be formed from the reaction of $RuCl_3$ and dithiocarbamates, indeed many studies have reported mixtures of paramagnetic $[Ru(S_2CNR_2)_3]$ and diamagnetic $[Ru_2(S_2CNR_2)_5]^+$ (which can exist in two isomeric forms) from these reactions.[229–232] Thus, it may be that such diamagnetic cations are the real products of the reactions described above.[226–228] Akin to their ruthenium analogues, osmium complexes, [Os

($S_2CNR_2)_3$], are also low spin d^5 systems that show resonances across a wide chemical shift range in their ^{1}H NMR spectra and are easily oxidised.[233]

(iii) Stable dithiocarbamate complexes of high-valent metal oxides are always accessible

One of the major benefits of the dithiocarbamate ligand is its ability to stabilise metals in a wide range of oxidation states, being (in simple terms) attributed to the accessibility of dithiocarbamate and thioureide resonance forms. Thus, the former is a relatively *soft* (strong field) and the latter a *hard* (weak field) donor. While not unique to dithiocarbamates, some ligand sets, for example the related xanthates ($ROCS_2^-$), cannot adopt the latter form as the oxygen is too electronegative to act as an electron-pair donor.[234] Adoption of the thioureide form also accounts for the partial double bond character of the backbone C–N vector which leads to hindered rotation about it.[235] Thus, rotamers of complexes [$M(S_2CNR^1R^2)_2$] (M = Ni, Pd) can be distinguished, and their rate of interconversions measured.[236] The thioureide form can also account for the stability of high-valent species such as of Mo(VI) and W(VI) complexes.[8,9] However, one should not forget that the dithiocarbamate is redox active, being relatively easily oxidised, and thus when bound to a highly oxidised metal centre, the system is on a cliff edge, as beautifully illustrated by a series of publications from Stiefel and co-workers.[237–241]

While a wide range of metal centres and oxidation states can be tolerated by dithiocarbamates,[8] this does not extend to the most oxidising. For example, reaction of dithiocarbamate salts with potassium dichromate, $K_2[Cr_2O_7]$, affords a mixture of two Cr(III) products: ring-expanded [$Cr(S_2CNR_2)_2(OS_2CNR_2)$] as the major component together with [$Cr(S_2CNR_2)_3$] (R = Me, Et)[242] (Fig. 24). Thus, (at least formally) three equivalents of dithiocarbamate act as one-electron reducing agents and the other three as ligands. The precise mode of formation of the ring-expanded complex is not clear. In related work, Farmer and co-workers showed that addition of H_2O_2 to [Ru(κ^2-2,2′-bipy)$_2$(S_2CNMe_2)]$^+$ afforded both ring-expanded sulfur-oxidised isomers but they did not interconvert, suggesting that they are formed *via* two separate pathways,[243] although in other work they showed that [$Zn(S_2CNEt_2)(OS_2CNEt_2)$] was a product of the oxygenation of [$Zn(S_2CNEt_2)_2$], a transformation that can be reversed upon addition of a phosphine.[244] Interestingly, reaction of chromate with excess dithiocarbamate has been repurposed as an analytical method of measuring relative amounts of Cr(III) and Cr(IV).[245–247] Thus, Cr(III) reacts to form [$Cr(S_2CNR_2)_3$] and Cr(VI) a mixture of this and the ring-expanded products. Importantly the two products have different chromatographic retention times and thus by understanding the precise ratio of products formed from the Cr(VI) reaction it is possible to determine relative amounts of Cr(III) and Cr(VI), although not all publications seem to do it this way, with some suggesting that Cr(III) is unreactive towards dithiocarbamates.

Likely dithiocarbamates cannot stabilise high oxidation states such as Os(VIII) and Re(VII), since these metal centres are powerful oxidising agents. There are reports of Os(VI) dithiocarbamate complexes, *trans*-[$OsO_2(S_2CNR_2)_2$],[248,249] which show distinctive vibrations at 839 and 888 cm^{-1} in the IR spectrum, being assigned to asymmetric and symmetric *trans*-OsO_2 vibrations respectively.[249] Further investigations are needed to unequivocally establish the validity of these claims, but they seem quite likely to be correct given that the *trans*-[Os(VI)O_2] moiety is particularly stable, being found for example in complexes such as *trans*-[$OsO_2(CO)_4$]$^{2+}$ and *trans*-[$OsO_2(OH)_4$]$^{2-}$.

(iv) Au(III) complexes, [$Au(S_2CNR_2)_2$]$^+$ and [$AuCl_2(S_2CNR_2)$], are easily prepared in their pure forms

Gold(III) dithiocarbamate complexes of the type [$AuX_2(S_2CNR_2)$] (where X = Cl, Br, I) have been widely studied as potential anti-cancer metallo-pharmaceuticals. Structurally they are comparable to *cis*-platin and the mechanism of action is suspected to be similar.[250] These compounds were first synthesised in 1964 by oxidation of the Au(I) complex [Au(S_2CNR_2)]$_n$ with elemental X_2.[251] This supposedly afforded the Au(III) dithiocarbamate [$AuX_2(S_2CNR_2)$] as a single compound in solution. Alternatively, the addition of one equivalent of dithiocarbamate to Au(III) halides is claimed to result in the sole formation of [$AuX_2(S_2CNR_2)$]. In a similar fashion, addition of two equivalents of dithiocarbamate to Au(III) halides supposedly resulted in the sole formation of the cationic complex [$Au(S_2CNR_2)_2$]$^+$.[9] Often in this system X^- is invoked as the counterion, but a haloaurate species is more likely to be present.

We recently investigated the [$AuX_2(S_2CNR_2)$] system thoroughly and discovered that the established reactivity is not correct.[252] The series of compounds [$AuX_2(S_2CNR_2)$] where X = halide cannot be isolated as a single species in solution; instead, they exist in an equilibrium with [$Au(S_2CNR_2)_2$][AuX_4] (Fig. 25). This equilibrium is present irrespective of the method of synthesis, or the ratio of dithiocarbamate to Au(III). A careful look at the older literature reveals that this equili-

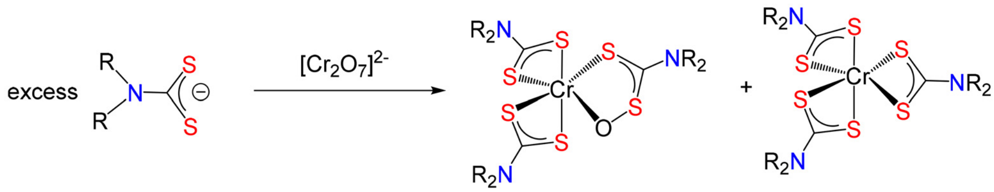

Fig. 24 Cr(III) complexes from reaction of dithiocarbamates and $K_2[Cr_2O_7]$.

brium has always been present even though it had not previously been acknowledged. For example, the ^{1}H and ^{13}C{^{1}H} NMR spectra of dibenzyl-dithiocarbamate- and methyl-sarcosine-dithiocarbamate-derived Au(III) complexes both clearly show the presence of two dithiocarbamate environments, one for the neutral species and one for the ion pair.[253,254] Mass spectrometry of $[AuX_2(S_2CNR_2)]$ revealed that the cation $[Au(S_2CNR_2)_2]^+$ was also present in the sample, although it was explained as decomposition in solution.[255] A single crystal containing $[AuCl_2(S_2CNiPr_2)]$, two $[Au(S_2CNiPr_2)_2]^+$ cations and two $[ClO_4]^-$ anions was obtained, showing that both components of the equilibrium were present in a single reaction mixture.[256] Recently, it was shown that an equilibrium mixture where $[Au(S_2CNiPr_2)_2][AuCl_4]$ was the majority product could be converted to a mixture where $[AuCl_2(S_2CNiPr_2)]$ was the majority product by refluxing in acetone.[257]

We note here that it is possible to obtain $[Au(S_2CNR_2)_2]^+$ as a single species in solution, but the counterion must be chosen with care and haloaurate anions should be avoided. For example, use of a weakly coordinating anion such as $[BF_4]^-$ led to the isolation of $[Au(S_2CNR_2)_2][BF_4]$ which showed no sign of existing as an equilibrium, even upon standing in solution for several weeks. However, as soon as the anion was metathesized to $[AuCl_4]^-$, the equilibrium restarted.[252] In a similar vein, it is possible to isolate $[AuX_2(S_2CNR_2)]$ as a single pure product in solution by avoiding the use of halide ions: stable systems are known to exist for X = Me, C_6F_5, mesityl and thiolate, for example.[258–261]

The above notwithstanding, it is possible to fractionally crystallise $[AuX_2(S_2CNR_2)]$ as a single compound. The neutral species forms orange crystals (in contrast to the ion pair, which is yellow); these are indefinitely stable in the solid phase, but as soon as the crystals are dissolved in an organic solvent then the equilibration process resumes. Researchers are urged to be cautious here by not mistaking this for a single pure product in solution.[261] It is also noteworthy that elemental analysis is not a useful characterization technique since the two components of the equilibrium, namely $[AuX_2(S_2CNR_2)]$ and $[Au(S_2CNR_2)_2][AuX_4]$, have identical empirical formulae and cannot be used to distinguish the two isomers.[262]

(v) Primary amine-derived dithiocarbamate complexes are always stable

The majority of dithiocarbamate chemistry focuses on those derived from secondary amines. There are several reasons for this, one being their greater stability *vs.* those derived from primary amines. Thus, while all dithiocarbamates are unstable in acidic media, the relatively acidic nature of the unique proton in $RNHCS_2^-$ also makes them prone to instability in basic media. Nevertheless, there are some relatively simple and highly reproducible syntheses of primary amine dithiocarbamate salts. Examples of these are group 10[263–265] and group 12[266–269] $[M(S_2CNHR)_2]$ complexes, but also $[Co(S_2CNHR)_3]$[270,271] and ^{99m}Tc complexes with radiopharmaceutical applications.[272–274] The authenticity of homoleptic primary amine dithiocarbamate complexes of other metals is far less certain and likely the majority are too unstable to be isolated.

Upon metal binding the acidity of the backbone proton is retained, its removal generating the dianionic dithiocarbimate (or imidomethanedithiolate) ligand, $S_2C{=}NR^{2-}$. Such ligands form complexes with a wide range of metals,[103] being especially prevalent for Group 10 elements and when the substituent is strongly electron-withdrawing, for example aryl or cyanide. For Group 10 elements, as discussed earlier (Fig. 8), double deprotonation upon addition of a strong base of $[M(S_2CNHAr)_2]$ and $[M(S_2CNHR)_2]$ affords the corresponding dithiocarbimate dianions that, provided they are kept under anhydrous and oxygen-free conditions, have significant lifetimes and can be used to prepare functionalised dithiocarbamate derivatives. Stability of the dithiocarbimate complexes (presumably) results from delocalisation of the excess electron density into the vacant d-orbital. However, this is not the case for most other metals. For example, addition of base to Group 12 complexes $[M(S_2CNHR)_2]$ and $[M(S_2CNHAr)_2]$ (M = Zn, Cd) results in rapid decomposition to give ZnS or CdS nanomaterials.[266–268] Indeed, this is advantageous, as is the case for $[Ni(S_2CNHR)_2]$[275] as they provide low temperature routes to these nanomaterials (Fig. 26).

For organic chemists reading this it may ring bells as the base-induced decomposition of primary amine dithiocarbamates to afford organic isothiocyanates is a well-developed preparative method.[276–278] Indeed, often a metal ion is added to facilitate the process. Thus, such complexes are not stable, certainly under basic conditions, rapidly decomposing to afford the isothiocyanate. Nevertheless, there are (purported) examples of $[Fe(S_2CNHR)_3]$[279,280] and $[Cu(S_2CNHR)_2]$[281–285] in the literature, some of the latter being touted as enzyme inhibitors.[285] We have recently looked more closely at both systems in our laboratory and will publish our results in due course. The iron system is complex and is not appropriate to discuss here, but $[Fe(S_2CNHR)_3]$ have at best a fleeting stabi-

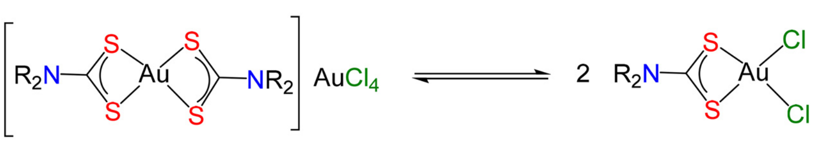

Fig. 25 Equilibrium between $[Au(S_2CNR_2)_2][AuCl_4]$ and $[AuCl_2(S_2CNR_2)]$.

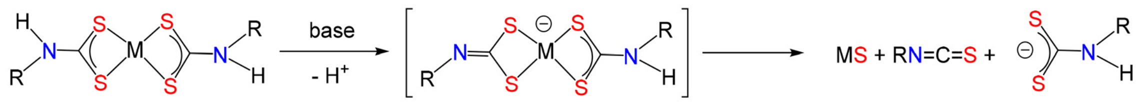

Fig. 26 Base-induced decomposition of $[M(S_2CNHR)_2]$ to afford RNCS and nanoscale metal sulfides.

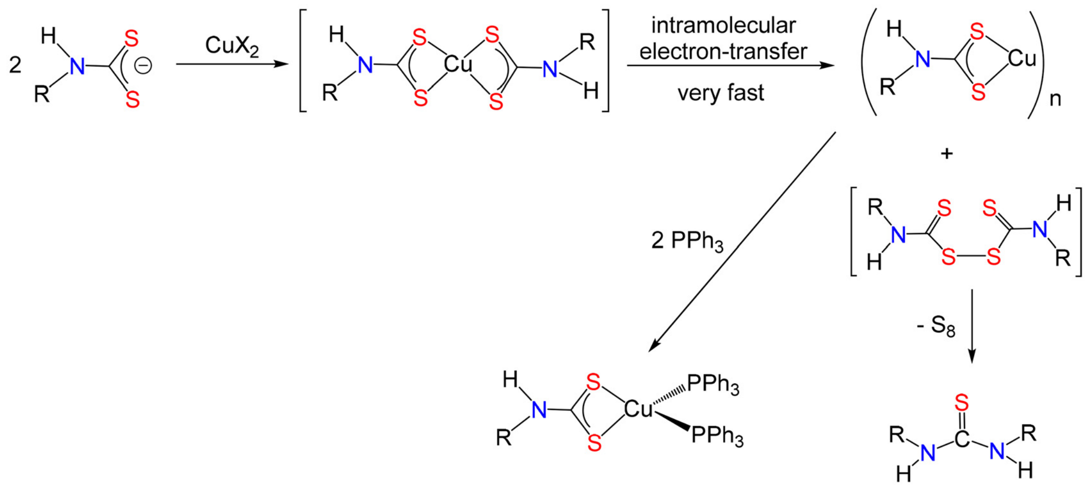

Fig. 27 Formation of $[Cu(S_2CNHR)]_n$ and subsequent reaction with PPh_3.

lity. Reactions of copper(II) salts with a range of primary amine derived dithiocarbamates in water leads to isolation of high yields of bright yellow polymeric Cu(I) complexes, $[Cu(S_2CNHR)]_n$ (R = Bu, Cy) along with the corresponding thiourea.[286] Their poor solubility hinders full characterisation, but simple addition of a slight excess of PPh_3 affords the soluble and crystallographically characterised complexes, $[Cu(S_2CNHR)(PPh_3)_2]$[286] (Fig. 27). In this regard we note that $[Cu(S_2CNHPh)(PPh_3)_2]$ has previously been prepared from reaction of $[Cu(BH_4)(PPh_3)_2]$ with PhNCS.[287] Thus, primary amine dithiocarbamates are stable at a Cu(I) centre but not Cu(II).

We briefly note here that $[NH_4][S_2CNH_2]$ is easily prepared[288,289] and has been used to generate a range of stable homoleptic complexes, including crystallographically characterised: $[Ni(S_2CNH_2)_2]$,[290] $[Zn(S_2CNH_2)_2]$,[291] $[Cr(S_2CNH_2)_3]$,[292] $[Co(S_2CNH_2)_3]$,[288,293] $[Rh(S_2CNH_2)_3]$,[288] $[Ag(S_2CNH_2)]$,[294] $[Au(S_2CNH_2)]$,[295] $[Au(S_2CNH_2)_2][SCN]$,[296] $[Cu(S_2CNH_2)]$[297] and $[Cu(S_2CNH_2)_2][NH_4]$.[297] Considering the discussion above, the finding that this ligand is only stabilised at the Cu(I) centre is interesting. Further several non-homoleptic Ru(II) derivatives have been prepared and crystallographically characterised[288] suggesting that there is a relatively rich coordination chemistry of this ligand still to be explored.

(v) Complexes with two different dithiocarbamate ligands and dithiocarbamate-containing mixed-ligand complexes are (easily) accessible in a pure state

Many homoleptic dithiocarbamate complexes are known, being easy to prepare even in the most basic of laboratory settings.[8,9] In developing this chemistry further, it is tempting to consider preparing related complexes in which two (or more) different dithiocarbamates bind to a single metal centre, thus providing easy tuning of chemical and physiochemical properties. Consequently, over the past decade, there has been an increasing number of publications claiming the formation of pure complexes containing two different dithiocarbamate ligands of Ni(II),[298] Cu(II),[299–301] zinc and mercury[302–306] and other transition metal[307–309] and main group[310–315] elements. In all these reports, the simple addition of equimolar equivalents of two different dithiocarbamates to a metal salt is reported to (cleanly) afford the mixed-ligand complex, without any explanation as to why a mixed-ligand complex might be thermodynamically preferable to either the two homoleptic complexes or a statistical mixture of homo- and heteroleptic complexes. Very few of these reports are supported with single crystal X-ray data, or compelling characterising data. Crystal structures of $[Hg(S_2CNMePh)(S_2CNEtPh)]$[304] and $[Zn(S_2CNMePh)(S_2CNEtPh)(2,2'\text{-bipy})]$[305] are in the literature but in both there is a significant disorder of the Me/Et groups. The only good quality (non-disordered) example of a molecular structure of a heteroleptic dithiocarbamate complex is that of the anion $[Cd(S_2CNPr_2)_2(S_2CNMeBu)]^-$, formed (in a similar manner to other examples) upon addition of pyrrolidinium salts of $[S_2CNMeBu]^-$ to $[Cd(S_2CNPr_2)_2]$.[316] However, while the crystal structure shows a well-ordered mixed-dithiocarbamate complex, both ^1H and $^{13}C\{^1H\}$ NMR spectra show that in solution multiple products are present, resulting from ligand-exchange. Thus, while complexes with two different dithiocarbamates are accessible as part of a mixture and can (at least potentially) be selectively crystallised out, they are not accessible in pure form in solution.

For diamagnetic species, NMR spectroscopy should be a simple way of probing such equilibria, however, the (relatively) slow timescale coupled with low intensity of the quaternary backbone carbon signal in the $^{13}C\{^1H\}$ NMR spectrum and its insensitivity to substituent changes[317] renders it unsuitable. In contrast, HPLC has been shown to be an excellent analytical tool for investigating these systems, being used effectively, for example, by Moriyasu and Hashimoto,[318–320] Liska and co-workers[321,322] and others.[323] Thus, Moriyasu and Hashimoto mixed homoleptic bis(dithiocarbamate) complexes of nickel and copper (which can't easily be studied by NMR spectroscopy) and in all cases found that they were labile and in equilibrium with the mixed-ligand counterpart (Fig. 28). Rate constants depend on both metal and substituents, for Ni(II) being of the order of 10^1–10^2 M^{-1} s^{-1} and for Cu(II) slower at *ca.* 10^3 M^{-1} s^{-1}.[317–320] These studies were later extended to other metals and in all cases, the dithiocarbamates were found to be labile with equilibrium constants being *ca.* 4, *i.e.* a statistical mixture of the three complexes.[324] Similar equilibria have also been noted between homoleptic nickel complexes of primary and secondary amines, affording $[Ni(S_2CNR^1{}_2)(S_2CNHR^2)]$,[318–320] and also between $[Ni(S_2CNR_2)_2]$ and xanthate complexes, $[Ni(S_2COR)_2]$.[325] Most studies support a bimolecular exchange process likely proceeding through a dimeric intermediate, the form of which is common in crystallographic studies of $[Zn(S_2CNR_2)_2]$ and $[Cu(S_2CNR_2)_2]$.[8] Rapid dithiocarbamate exchange has also been noted at Fe(III)[326–328] and Hg(II)[329,330] centres.

For low spin d^6 $[Co(S_2CNR_2)_3]$ complexes, the CFSE is so high that exchange rates are slow[331] and isolation of mixed-ligand complexes is possible. Thus, addition of a dithiocarbamate salt, $NaS_2CNR^1{}_2$ to $[Co_2(S_2CNR^2{}_2)_5]^+$ affords a mixture of $[Co(S_2CNR^1{}_2)(S_2CNR^2{}_2)_2]$ and $[Co_2(S_2CNR^2{}_2)_3]$[332] (Fig. 29). Further, adding equimolar amounts of two different dithiocarbamates to Co(III) salts in water affords a statistical mixture of products,[333] and a similar mixture of products can be obtained upon heating equimolar amounts of $[Co(S_2CNEt_2)_3]$ and $[Co(S_2CN^iPr_2)_3]$ either in the solid-state or at 155 °C in chloronaphthalene for 4–5 h.[333] Importantly, these mixtures can be fully separated by column chromatography allowing their individual characterisation. Interestingly, while it is hard to differentiate them by ^1H or $^{13}C\{^1H\}$ NMR spectroscopy, they can be distinguished by ^{59}Co NMR spectroscopy and mass spectrometry and have tuneable oxidation potentials.[333]

The ease of accessibility of mixed-ligand complexes containing dithiocarbamates also needs some careful consideration. There are many such examples[8,9] but for solution stability in their pure form they need to feature either a relatively non-labile metal centre with either bulky non-dithiocarbamate ligands that preclude formation of a bimetallic intermediate or secondary inter-ligand interactions (*e.g.* hydrogen-bonding). Following on from the discussion above, Co(III) is a good example of a non-labile metal centre. Thus, $[Co_2(S_2CNR_2)_5]^+$ reacts with a range of nucleophiles to afford $[Co(S_2CNR_2)_3]$ and a mixed-ligand complex, a recent case being the formation of Co(III) bis(dithiocarbamate)dithiolane complexes from addition of dithiones (Fig. 29).[334] Other examples of a high CFSE leading to stable mixed-ligand complexes relate to the iron dithietane complexes[189] (Fig. 20) which exist in temperature-dependent spin-equilibrium between the singlet (S = 0) ground state and a low-lying triplet (S = 1) excited state. Thus, not only are these mixed-ligand complexes stable, but their NMR spectra are also accessible.

However, simultaneously adding a dithiocarbamate and a different ligand to a metal salt will not automatically afford the mixed-ligand species as has been suggested in several publications.[335–338] Just as for complexes with two different dithiocarbamates, it is hard by simple spectroscopic methods to tell the difference between a 1 : 1 mixture of two homoleptic complexes and a mixed-ligand species, and in many cases the three likely co-exist. A recent publication highlights this nicely (Fig. 30).[339] Thus, while insertion of an imide group into a Ni–S bond of $[Ni(S_2CNR_2)_2]$ affords mixed-ligand complexes, examples of which can be crystallographically characterised,

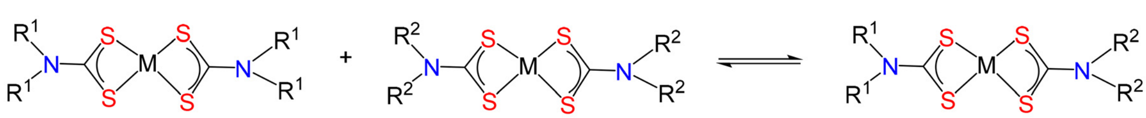

Fig. 28 Equilibrium between homoleptic and mixed ligand bis(dithiocarbamate) complexes.

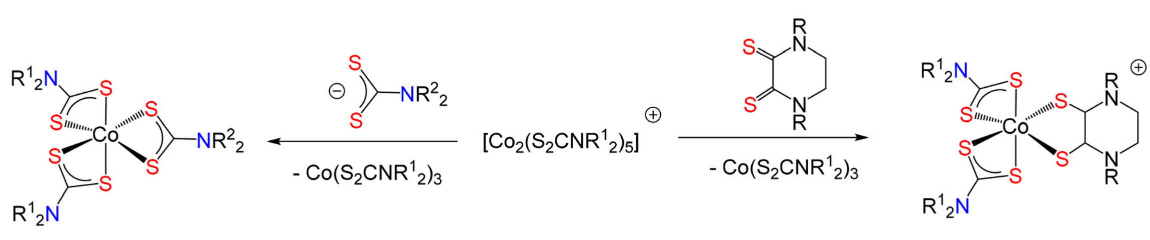

Fig. 29 Synthesis of heteroleptic Co(III) dithiocarbamate complexes.

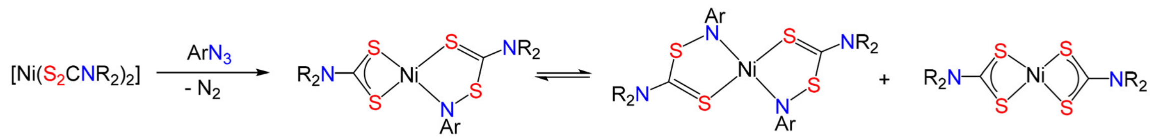

Fig. 30 Formation of mixed-ligand complex in equilibrium with homoleptic complexes.

upon dissolution they are shown to be in equilibrium with the two homoleptic complexes.

(vi) Reacting two different dithiocarbamate complexes gives a pure mixed metal product

Given the extremely large number of homonuclear transition metal dithiocarbamate complexes that are known, it is perhaps surprising that dithiocarbamate-bridged heteronuclear complexes are rare. Thus, as shown by Robinson,[340] complexes obtained by successive addition of metal salts MX_2 (M = Zn, Cd or Hg) and $M'Y_2$ (M′ = VO, Mn, Fe, Co, Ni, Cu or Zn) to a solution of a sodium dithiocarbamate are not heterobimetallic $[\{M'M(S_2CNR_2)_4\}_n]$ but rather contain a mixture of homonuclear complexes. Likewise, reactions of Pd(II) salts $[PdCl_2L_2]$ (L = PhCN, L_2 = dppe) with a series of homoleptic dithiocarbamate complexes affords palladium-dithiocarbamate cations $[Pd(S_2CNR_2)L_2]^+$ with the second metal being incorporated into the counterion.[341–343] More recently, Torimoto and co-workers added $Na(S_2CNEt_2)$ to mixtures of metal salts and used the ensuing "complex" as a precursor to a range of nanoscale metal sulfides with quantum dot properties.[344–347] While the method is effective and efficient, the suggestion that a mixed-metal complex is formed is erroneous. Rather the precursor "complex" is an intimate mixture of several different complexes. There are some well-authenticated examples of dithiocarbamate-bridged heterobimetallic complexes, being especially prevalent amongst the coinage metals[348–351] and there are also a small number of other dithiocarbamate-containing heteronuclear complexes that have been crystallographically characterised.[352,353] Nevertheless, the vast majority of dithiocarbamate complexes contain a single metal type.

6. Dithiocarbamate complexes as single source precursors

Dithiocarbamate complexes find widespread use as single source precursors for a range of nanoscale and thin film metal sulfides.[49–52] Thus, simply heating, either in the solid-state or solution, the complex or mixture of complexes, results in S–C and other bond scission(s) affording the thermodynamically stable metal-sulfide(s) and various organic species, the latter (normally) being easily removed either by washing or evaporation. The utility of this simple approach is that air-stable dithiocarbamate complexes from across the periodic table can be (relatively easily) prepared and stored, and by judicious control of reaction conditions and stoichiometry a wide range of binary, ternary and quaternary metal sulfides can be accessed. A nice example of this is their use towards the synthesis of Cu_2ZnSnS_4 (CZTS) a quaternary semiconductor with a power conversion efficiency of *ca.* 10% that has been suggested as a viable material for thin film solar cells. Thus, decomposing mixtures of copper, zinc and tin dithiocarbamates leads to the formation of CZTS thin films or quantum dots.[354,355]

However, such transformations are not as simple as they might appear. Firstly, in the solid state, thermogravimetric analysis studies have shown that temperatures of between 200–400 °C are required to cleave the S–C (and other) bonds within dithiocarbamate complexes.[356–359] Decomposition temperatures can be tuned (normally within a small range) upon changing substituents, and there is also a correlation between the ease of thermal decomposition and ionic radius of the metal ion; the smaller the metallic ionic radius, the greater the thermal stability.[360] In solution, decomposition temperatures can be significantly lower than in the solid-state.[275,361,362] For example, the water-soluble SSP $[Cu\{S_2CN(CH_2CO_2H)_2\}_2]$ decomposes at 180 °C in the solid state but at *ca.* 80 °C in water.[362] Another issue to address when preparing ternary, quaternary or multinary sulfides, is matching of decomposition temperatures, such that all SSPs decompose within a relatively small range, thus ensuring that the different molecular building blocks are all available at the nucleation stage. This is nicely exemplified by O'Brien's synthesis of CZTS.[363,364] Thus, as the decomposition temperature of $[Sn(S_2CNEt_2)_2]$ (174 °C) is significantly lower than those of $[Cu(S_2CNEt_2)_2]$ (220 °C) and $[Zn(S_2CNEt_2)_2]$ (240 °C), heating this mixture will lead to the premature formation of tin sulfides and hence the tin precursors was replaced by the Sn(IV) SSPs, $[Sn(S_2CNBu_2)_4]$[363] and $[Bu_2Sn(S_2CNBu_2)_2]$[364] which decompose at higher temperatures. A study by Torimoto and co-workers nicely highlights the need to carefully control decomposition conditions.[365] Thus, for the synthesis of $Ag(In_xGa_{1-x})S_2$ quantum dots, simply heating a mixture of silver, indium and gallium precursors initially results in formation of polydisperse Ag_2S as the silver dithiocarbamate decomposes at lower temperatures than others, and upon further heating as indium and gallium SSPs decompose they give a shell of these sulfides around the Ag_2S (Fig. 31a).[366] However, when a silver source is injected into the decomposition reaction then co-nucleation of all components occurs, initially to give a core–shell structure, while further heating affords the desired ternary phase sulfide as quantum dots.[365]

Given these complications and constraints, it is surprising that there are an increasing number of reports seemingly suggesting that simply preparing mixtures of dithiocarbamates at room temperature results in the formation of metal sulfides

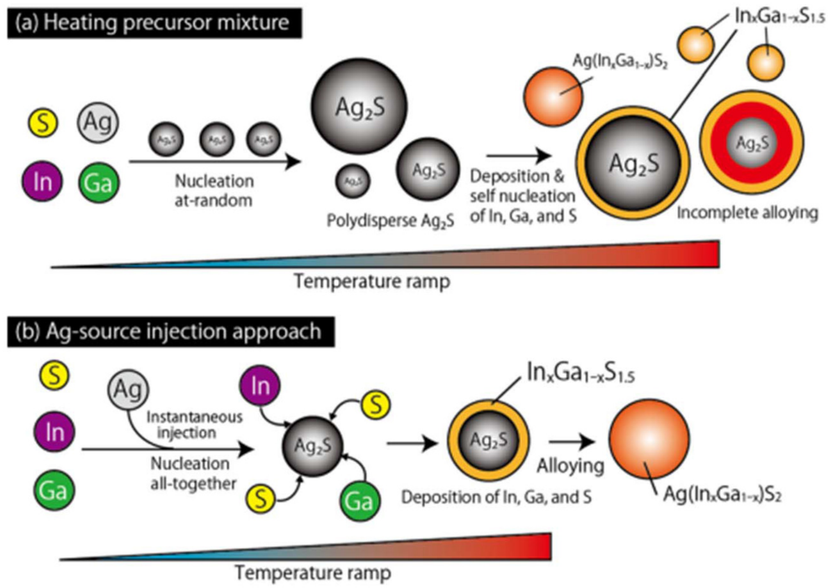

Fig. 31 Schematic illustrations of the synthesis of $Ag(In_xGa_{1-x})S_2$ quantum dots form (a) heating of the precursor mixture and (b) injecting a silver source into the decomposition mixture.[365]

i.e. there is no mention of a heating or other decomposition process[367–371] although decomposition appears to be supported by powder X-ray diffraction data. Further, many of these "decompositions" are proposed to give composite mixtures of individual metal sulfides, some of which such as BaS_3, are normally prepared at 400 °C.[372] Clearly such reports require some scrutiny and perhaps further explanation(s) from the authors.

7. Summary and conclusions

In this perspective we have tried to address common misconceptions and errors that we have found in the literature on dithiocarbamates and their complexes. Amongst the challenges faced by those working in this area are the vast number of publications and patents, and the widespread reach of this simple ligand type across many different fields of research. Thus, it is hard for anyone to fully keep up to date and understand all aspects of their chemistry. Likely many misconceptions-errors that have crept into the literature result are further exacerbated by the recent (seemingly unstoppable) proliferation of scientific journals. It is a testament to the wide applicability of dithiocarbamate chemistry that this perspective cites over 200 different journal titles: some of us long for the days when our library reading covered 10–15 journals, each with a clear remit. Thus, we need to understand that newcomers to this mature field of research have a lot of reading and understanding to do to get up to speed with what has gone before. Dithiocarbamate chemistry has been an active area of research for over 150 years and unlike some fields of scientific research, some early papers have relevance today. For example, while recently developing a primary-amine derived dithiocarbamate as a H_2S release-vector we came across a paper from 1891[373] which had effectively already studied this and provided us with invaluable insight into our work.

Having said this, there is also some evidence of tardy work in the dithiocarbamate literature, with researchers either cutting corners, or not being totally honest in reporting their findings-data. Sadly, this appears to be an issue that has proliferated through all aspects of scientific research and one that seriously undermines the efforts of those who play fair. It is hard to understand why anyone would deliberately mis-represent their work, but undoubtably the high speed of modern living and (sometimes) excessive pressures put on academics to publish may be part of the problem. Linking publication to financial gain or making it a pre-requisite for promotion will tempt some to cut corners.

Conflicts of interest

There are no conflicts to declare.

Data availability

There is no data associated with this submission.

Acknowledgements

We thank Dr Jagodish C. Sarker for reading through the manuscript and providing valuable comments, and Dr Shishir Ghosh for attempting to reproduce a reaction discussed herein.

References

1 C. Campanale, M. Triozzi, A. Ragonese, D. Losacco and C. Massarelli, Dithiocarbamates: Properties, Methodological Approaches and Challenges to Their Control, *Toxics*, 2023, **11**, 851.
2 J. M. Veiga-del-Bano, S. Martinez-Lopez, G. Perez-Lucas, J. J. Cuenca-Martinez and P. Andreo-Martinez, Trends in dithiocarbamates food research: A bibliometric vision, *Chemosphere*, 2023, **313**, 137342.
3 R. J. Magee and J. O. Hill, The analytical chemistry of metal dithiocarbamate complexes, *Rev. Anal. Chem.*, 1985, **8**, 5–72.
4 L. Ye, A. T. Dinkova-Kostova, K. L. Wade, Y. Zhang, T. A. Shapiro and P. Talalay, Quantitative determination of dithiocarbamates in human plasma, serum, erythrocytes and urine: pharmacokinetics of broccoli sprout isothiocyanates in humans, *Clin. Chim. Acta*, 2002, **316**, 43–53.
5 K. W. Bruland, R. P. Franks, G. A. Knauer and J. H. Martin, Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water, *Anal. Chim. Acta*, 1979, **105**, 233–245.
6 C. Yuan, B. Liu, F. Liu, M.-Y. Han and Z. Zhang, Fluorescence "Turn On" Detection of Mercuric Ion Based on Bis(dithiocarbamato)copper(II) Complex Functionalized Carbon Nanodots, *Anal. Chem.*, 2014, **86**, 1123–1130.
7 O. H. J. Szolar, Environmental and pharmaceutical analysis of dithiocarbamates, *Anal. Chim. Acta*, 2007, **582**, 191–200.
8 G. Hogarth, Transition metal dithiocarbamates: 1978–2003, *Prog. Inorg. Chem.*, 2005, **53**, 71–561.
9 D. Coucouvanis, The chemistry of the dithioacid and 1,1-dithiolate complexes, 1968–1977, *Prog. Inorg. Chem.*, 1979, **26**, 301–469.
10 P. J. Heard, Main group dithiocarbamate complexes, *Prog. Inorg. Chem.*, 2005, **53**, 1–69.
11 F. Bonati and R. Ugo, Organotin(IV) *N*,*N*-disubstituted dithiocarbamates, *J. Organomet. Chem.*, 1967, **10**, 257–268.
12 E. R. T. Tiekink, Tin dithiocarbamates: applications and structures, *Appl. Organomet. Chem.*, 2008, **22**, 533–550.
13 G. Hogarth and D. C. Onwudiwe, Copper Dithiocarbamates: Coordination Chemistry and Applications in Materials Science, Biosciences and Beyond, *Inorganics*, 2021, **9**, 70.
14 A. M. Bond and R. L. Martin, Electrochemistry and redox behavior of transition metal dithiocarbamates, *Coord. Chem. Rev.*, 1984, **54**, 23–98.
15 Y. S. Tan, C. I. Yeo, E. R. T. Tiekink and P. J. Heard, Dithiocarbamate Complexes of Platinum Group Metals: Structural Aspects and Applications, *Inorganics*, 2021, **9**, 60.
16 J. Cookson and P. D. Beer, Exploiting the dithiocarbamate ligand in metal-directed self-assembly, *Dalton Trans.*, 2007, 1459–1472.
17 A. Torres-Huerta, B. Rodriguez-Molina, H. Hopfl and M. A. Garcia-Garibay, Synthesis and Solid-State Characterization of Self-Assembled Macrocyclic Molecular Rotors of Bis(dithiocarbamate) Ligands with Diorganotin (IV), *Organometallics*, 2014, **33**, 354–362.
18 E. R. T. Tiekink, On the coordination role of pyridyl-nitrogen in the structural chemistry of pyridyl-substituted dithiocarbamate ligands, *Crystals*, 2021, **11**, 286.
19 L. Monser and N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, *Sep. Purif. Technol.*, 2002, **26**, 137–146.
20 M. Tuzen, K. O. Saygi and M. Soylak, Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes, *J. Hazard. Mater.*, 2008, **152**, 632–639.
21 P. I. Girginova, A. L. Daniel-da-Silva, C. B. Lopes, P. Figueira, M. Otero, V. S. Amaral, E. Pereira and T. Trindade, Silica coated magnetite particles for magnetic removal of Hg^{2+} from water, *J. Colloid Interface Sci.*, 2010, **345**, 234–240.
22 S. Kanchi, P. Singh and K. Bisetty, Dithiocarbamates as hazardous remediation agent: A critical review on progress in environmental chemistry for inorganic species studies of 20th century, *Arabian J. Chem.*, 2014, **7**, 11–25.
23 K. Nakakubo, M. Endo, Y. Sakai, F. B. Biswas, K. H. Wong, A. S. Mashio, T. Taniguchi, T. Nishimura, M. Katsuhiro and H. Hasegawa, Crosslinked dithiocarbamate-modified cellulose with enhanced thermal stability and dispersibility as a sorbent for arsenite removal, *Chemosphere*, 2022, **307**, 135671.
24 G. Hogarth, Metal-dithiocarbamate complexes: chemistry and biological activity, *Mini-Rev. Med. Chem.*, 2012, **12**, 1202–1215.
25 C. Nardon, G. Boscutti and D. Fregona, Beyond platinums: gold complexes as anticancer agents, *Anticancer Res.*, 2014, **34**, 487–492.
26 L. Ronconi, L. Giovagnini, C. Marzano, F. Bettio, R. Graziani, G. Pilloni and D. Fregona, Gold Dithiocarbamate Derivatives as Potential Antineoplastic Agents: Design, Spectroscopic Properties, and in Vitro Antitumor Activity, *Inorg. Chem.*, 2005, **44**, 1867–1881.
27 L. Ronconi, C. Marzano, P. Zanello, M. Corsini, G. Miolo, C. Macca, A. Trevisan and D. Fregona, Gold (III) Dithiocarbamate Derivatives for the Treatment of Cancer: Solution Chemistry, DNA Binding, and Hemolytic Properties, *J. Med. Chem.*, 2006, **49**, 1648–1657.
28 F. K. Keter, I. A. Guzei, M. Nell, W. E. van Zyl and J. Darkwa, Phosphinogold(I) Dithiocarbamate Complexes: Effect of the Nature of Phosphine Ligand on Anticancer Properties, *Inorg. Chem.*, 2014, **53**, 2058–2067.
29 J. O. Adeyemi and D. C. Onwudiwe, Organotin(IV) dithiocarbamate complexes: chemistry and biological activity, *Molecules*, 2018, **23**, 1–27.
30 R. Schreck, B. Meier, D. N. Maennel, W. Droege and P. A. Baeuerle, Dithiocarbamates as potent inhibitors of

nuclear factor κB activation in intact cells, *J. Exp. Med.*, 1992, **175**, 1181–1194.

31 Q. W. Xie, Y. Kashiwabara and C. Nathan, Role of transcription factor NF-κB/Rel in induction of nitric oxide synthase, *J. Biol. Chem.*, 1994, **269**, 4705–4708.

32 M. Meyer, R. Schreck and P. A. Baeuerle, Hydrogen peroxide and antioxidants have opposite effects on activation of NF-κB and AP-1 in intact cells: AP-1 as secondary antioxidant-responsive factor, *EMBO J.*, 1993, **12**, 2005–2015.

33 N. Marui, M. K. Offermann, R. Swerlick, C. Kunsch, C. A. Rosene, M. Ahmad, R. W. Alexander and R. M. Medford, Vascular cell adhesion molecule-1 (VCAM-1) gene transcription and expression are regulated through an antioxidant-sensitive mechanism in human vascular endothelial cells, *J. Clin. Inhib. Med. Chem.*, 1993, **92**, 1866–1874.

34 C. T. Supuran, Structure-based drug discovery of carbonic anhydrase inhibitors, *J. Enzyme Inhib. Med. Chem.*, 2012, **27**, 759–772.

35 F. Carta, M. Aggarwal, A. Maresca, A. Scozzafava, R. McKenna and C. T. Supuran, Dithiocarbamates: a new class of carbonic anhydrase inhibitors. Crystallographic and kinetic investigations, *Chem. Commun.*, 2012, **48**, 1868–1870.

36 F. Carta, M. Aggarwal, A. Maresca, A. Scozzafava, R. McKenna, E. Masini and C. T. Supuran, Dithiocarbamates strongly inhibit carbonic anhydrases and show antiglaucoma action in vivo, *J. Med. Chem.*, 2012, **55**, 1721–1730.

37 D. J. Berry, R. T. Martin de Rosales, P. Charoenphun and P. J. Blower, Dithiocarbamate complexes as radiopharmaceuticals for medical imaging, *Mini-Rev. Med. Chem.*, 2012, **12**, 1174–1183.

38 R. Pasqualini, A. Duatti, E. Bellande, V. Comazzi, V. Brucato, D. Hoffschir, D. Fagret and M. Comet, Bis (dithiocarbamato) nitrido technetium-99 m radiopharmaceuticals: a class of neutral myocardial imaging agents, *J. Nucl. Med.*, 1994, **35**, 334–341.

39 R. T. Martin de Rosales, R. Tavare, R. L. Paul, M. Jauregui-Osoro, A. Protti, A. Glaria, G. Varma, I. Szanda and P. J. Blower, Synthesis of ^{64}CuII-Bis(dithiocarbamatebisphosphonate) and Its Conjugation with Superparamagnetic Iron Oxide Nanoparticles: In Vivo Evaluation as Dual-Modality PET-MRI Agent, *Angew. Chem., Int. Ed.*, 2011, **50**, 5509–5513.

40 R. T. A. Mayadunne, E. Rizzardo, J. Chiefari, Y. K. Chong, G. Moad and S. H. Thang, Living Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (RAFT Polymerization) Using Dithiocarbamates as Chain Transfer Agents, *Macromolecules*, 1999, **32**, 6977–6980.

41 G. Moad, E. Rizzardo and S. H. Thang, Radical addition-fragmentation chemistry in polymer synthesis, *Polymer*, 2008, **49**, 1079–1131.

42 M. Destarac, D. Charmot, X. Franck and S. Z. Zard, Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents, *Macromol. Rapid Commun.*, 2000, **21**, 1035–1039.

43 G. Moad, A Critical Survey of Dithiocarbamate Reversible Addition-Fragmentation Chain Transfer (RAFT) Agents in Radical Polymerization, *J. Polym. Sci., Part A: Polym. Chem.*, 2019, **57**, 216–227.

44 Y. Zhao, W. Perez-Segarra, Q. Shi and A. Wei, Dithiocarbamate Assembly on Gold, *J. Am. Chem. Soc.*, 2005, **127**, 7328–7329.

45 C. M. Wolff, P. D. Frischmann, M. Schulze, B. J. Bohn, R. Wein, P. Livadas, M. T. Carlson, F. Jaeckel, J. Feldmann, F. Wuerthner, *et al.*, All-in-one visible-light-driven water splitting by combining nanoparticulate and molecular co-catalysts on CdS nanorods, *Nat. Energy*, 2018, **3**, 862–869.

46 F. Dubois, B. Mahler, B. Dubertret, E. Doris and C. Mioskowski, A Versatile Strategy for Quantum Dot Ligand Exchange, *J. Am. Chem. Soc.*, 2007, **129**, 482–483.

47 E. R. Knight, A. R. Cowley, G. Hogarth and J. D. E. T. Wilton-Ely, Bifunctional dithiocarbamates: a bridge between coordination chemistry and nanoscale materials, *Dalton Trans.*, 2009, 607–609.

48 J. He, J. Liu, Y. Hou, Y. Wang, S. Yang and H. G. Yang, Surface chelation of caesium halide perovskite by dithiocarbamate for efficient and stable solar cells, *Nat. Commun.*, 2020, **11**, 4237.

49 J. C. Sarker and G. Hogarth, Dithiocarbamate Complexes as Single Source Precursors to Nanoscale Binary, Ternary and Quaternary Metal Sulfides, *Chem. Rev.*, 2021, **121**, 6057–6123.

50 D. Pan, L. An, Z. Sun, W. Hou, Y. Yang, Z. Yang and Y. Lu, Synthesis of Cu-In-S Ternary Nanocrystals with Tuneable Structure and Composition, *J. Am. Chem. Soc.*, 2008, **130**, 5620–5621.

51 M. A. Malik, N. Revaprasadu and P. O'Brien, Air-Stable Single-Source Precursors for the Synthesis of Chalcogenide Semiconductor Nanoparticles, *Chem. Mater.*, 2001, **13**, 913–920.

52 T. Trindade, P. O'Brien, X.-M. Zhang and M. Motevalli, Synthesis of PbS nanocrystallites using a novel single molecule precursors approach: X-ray single-crystal structure of $Pb(S_2CNEt\text{-}iso\text{-}Pr)_2$, *J. Mater. Chem.*, 1997, **7**, 1011–1016.

53 P. Tsvetkov, S. Coy, B. Petrova, M. Dreishpoon, A. Verma, M. Abdusamad, J. Rossen, L. Joesch-Cohen, R. Humeidi, R. D. Spangler, J. K. Eaton, E. Frenkel, M. Kocak, S. M. Corsello, S. Lutsenko, N. Kanarek, S. Santagata and T. R. Golub, Copper induces cell death by targeting lipoylated TCA cycle proteins, *Science*, 2022, **375**, 1254–1261.

54 D. Chen, Q. C. Cui, H. Yang and Q. P. Dou, Disulfiram, a Clinically Used Anti-Alcoholism Drug and Copper-Binding Agent, Induces Apoptotic Cell Death in Breast Cancer Cultures and Xenografts via Inhibition of the Proteasome Activity, *Cancer Res.*, 2006, **66**, 10425–10433.

55 D. Cen, D. Brayton, B. Shahandeh, F. L. Meyskens Jr. and P. J. Farmer, Disulfiram Facilitates Intracellular Cu Uptake

and Induces Apoptosis in Human Melanoma Cells, *J. Med. Chem.*, 2004, **47**, 6914–6920.
56 D. J. Lewis, P. Deshmukh, A. A. Tedstone, F. Tuna and P. O'Brien, On the interaction of copper(II) with disulfiram, *Chem. Commun.*, 2014, **50**, 13334–13337.
57 B. Cvek, V. Milacic, J. Taraba and Q. P. Dou, Ni(II), Cu(II), and Zn(II) Diethyldithiocarbamate Complexes Show Various Activities Against the Proteasome in Breast Cancer Cells, *J. Med. Chem.*, 2008, **51**, 6256–6258.
58 Z. Skrott, M. Mistrik, K. K. Andersen, S. Friis, D. Majera, J. Gursky, T. Ozdian, J. Bartkova, Z. Turi, P. Moudry, I. Vrobel, P. Pouckova, J. Sedlacek, A. Miklovicova, A. Kutt, J. Li, J. Mattova, C. Driessen, Q. P. Dou, J. Olsen, M. Hajduch, B. Cvek, R. J. Deshaies and J. Bartek, Alcohol-abuse drug disulfiram targets cancer via p97 segregase adaptor NPL4, *Nature*, 2017, **552**, 194–199.
59 Z. Skrott and B. Cvek, Diethyldithiocarbamate complex with copper: the mechanism of action in cancer cells, *Mini-Rev. Med. Chem.*, 2012, **12**, 1184–1192.
60 E. J. Ge, A. I. Bush, A. Casini, P. A. Cobine, J. R. Cross, G. M. DeNicola, Q. P. Dou, K. J. Franz, V. M. Gohil, S. Gupta, S. G. Kaler, S. Lutsenko, V. Mittal, M. J. Petris, R. Polishchuk, M. Ralle, M. L. Schilsky, N. K. Tonks, L. T. Vahdat, L. Van Aelst, D. Xi, P. Yuan, D. C. Brady and C. J. Chang, Connecting copper and cancer: from transition metal signalling to metalloplasia, *Nat. Cancer Rev.*, 2022, **22**, 102–113.
61 E. Ekinci, S. Rohondia, R. Khan and Q. P. Dou, Repurposing Disulfiram as An Anti-Cancer Agent: Updated Review on Literature and Patents, *Recent Pat. Anti-Cancer Drug Discovery*, 2019, **14**, 113–132.
62 Q. Yang, Y. Yao, K. Li, L. Jiao, J. Zhu, C. Ni, M. Li, Q. P. Dou and H. Yang, An Updated Review of Disulfiram: Molecular Targets and Strategies for Cancer Treatment, *Curr. Pharm. Des.*, 2019, **25**, 3248–3256.
63 X. Kang, S. Jadhav, M. Annaji, C.-H. Huang, R. Amin, J. Shen, C. R. Ashby Jr., A. K. Tiwari, R. J. Babu and P. Chen, Advancing Cancer Therapy with Copper/Disulfiram Nanomedicines and Drug Delivery Systems, *Pharmaceutics*, 2023, **15**, 1567.
64 Z. Skrott, D. Majera, J. Gursky, T. Buchtova, M. Hajduch, M. Mistrik and J. Bartek, Disulfiram's anti-cancer activity reflects targeting NPL4, not inhibition of aldehyde dehydrogenase, *Oncogene*, 2019, **38**, 6711–6722.
65 C. Wright and R. D. Moore, Disulfiram treatment of alcoholism, *Am. J. Med.*, 1990, **88**, 647–655.
66 J. Cobby, M. Mayersohn and S. Selliah, The rapid reduction of disulfiram in blood and plasma, *J. Pharmacol. Exp. Ther.*, 1977, **202**, 724–731.
67 J. C. Sarker, R. Nash, S. Boonrungsiman, D. Pugh and G. Hogarth, Diaryldithiocarbamates: Synthesis, oxidation to thiuram disulfides, Co(III) complexes $[Co(S_2CNAr_2)_3]$ and use as single source precursors to CoS_2, *Dalton Trans.*, 2022, **51**, 13061–13070.
68 J. C. Sarker, F. Alam, P. McNaughter, D. Pugh, J. K. Cockcroft, D. J. Lewis and G. Hogarth, Synthesis of diaryl dithiocarbamate complexes of zinc and their uses as single source precursors for nanoscale ZnS, *Inorg. Chim. Acta*, 2023, **556**, 121663.
69 J. C. Sarker, X. Xu, F. Alam, R. Nash, S. Boonrungsiman, D. Pugh, J. K. Cockcroft, D. J. Lewis and G. Hogarth, Copper diaryl-dithiocarbamate complexes and their application as single source precursors (SSPs) for copper sulfide nanomaterials, *New J. Chem.*, 2023, **47**, 12718–12727.
70 M. Kashif, A. G. Hogarth, Z. Khan, M. Imran and Z. Rehman, Platinum(II) dithiocarbamate complexes $[Pt(S_2CNR_2)Cl(PAr_3)]$ as anticancer and DNA-damaging agents, *Inorg. Chim. Acta*, 2020, **512**, 119853.
71 M. Imran, Z. Rehman, G. Hogarth, D. A. Tocher, G. Chaudhry, I. S. Butler, F. Belanger-Gariepy and T. Kondratyuk, Two new monofunctional platinum(II) dithiocarbamate complexes: phenanthriplatin-type axial protection, equatorial-axial conformational isomerism, and anticancer and DNA binding studies, *Dalton Trans.*, 2020, **49**, 15385–15396.
72 H.-U. Islam, A. Roffey, N. Hollingsworth, W. Bras, G. Sankar, N. H. De Leeuw and G. Hogarth, Understanding the role of zinc dithiocarbamate complexes as single source precursors to ZnS nanomaterials, *Nanoscale Adv.*, 2020, **2**, 798–807.
73 W.-D. Rudorf, Reactions of carbon disulfide with N-nucleophiles, *J. Sulfur Chem.*, 2007, **28**, 295–339.
74 A. A. Aly, A. B. Brown, T. M. I. Bedair and E. A. Ishak, Dithiocarbamate salts: biological activity, preparation, and utility in organic synthesis, *J. Sulfur Chem.*, 2012, **33**, 605–617.
75 Z.-Y. Wang, J. Li, N. Wang, H. Liu, W. Ding and K.-K. Wang, A Decade of Advances of CS_2/Amines in Three-Component Reactions, *Synthesis*, 2023, **55**, 1159–1171.
76 A. Z. Halimehjani, R. Mohtasham, A. Shockravi and J. Martens, Multicomponent synthesis of dithiocarbamates starting from vinyl sulfones/sulfoxides and their use in polymerization reactions, *RSC Adv.*, 2016, **6**, 75223–75226.
77 R. Biswas, P. Thakur, G. Kaur, S. Som, M. Saha, V. Jhajhria, H. Singh, I. Ahmed, B. Banerjee, D. Chopra, *et al.* Interfacial Engineering of $CuCo_2S_4$/g-C_3N_4 Hybrid Nanorods for Efficient Oxygen Evolution Reaction, *Inorg. Chem.*, 2021, **60**, 12355–12366.
78 A. A. Pradhan, M. C. Uible, S. Agarwal, J. W. Turnley, S. Khandelwal, J. M. Peterson, D. D. Blach, R. N. Swope, L. Huang, S. C. Bart, *et al.* Synthesis of $BaZrS_3$ and $BaHfS_3$ Chalcogenide Perovskite Films Using Single-Phase Molecular Precursors at Moderate Temperatures, *Angew. Chem., Int. Ed.*, 2023, **62**, e202301049.
79 B. Prelesnik, K. Andjelkovic, Z. Markovic, T. Sabo and S. Trifunovic, Potassium 3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 719–720.
80 R. Biswas, P. Thakur, G. Kaur, S. Som, M. Saha, V. Jhajhria, H. Singh, I. Ahmed, B. Banerjee, D. Chopra,

et al. Correction to Interfacial Engineering of $CuCo_2S_4$/g-C_3N_4 Hybrid Nanorods for Efficient Oxygen Evolution Reaction, *Inorg. Chem.*, 2022, **61**, 13226–13227.

81 J. D. E. T. Wilton-Ely, D. Solanki and G. Hogarth, Multifunctional dithiocarbamates as ligands towards the rational synthesis of polymetallic arrays: An example based on a piperazine-derived dithiocarbamate ligand, *Eur. J. Inorg. Chem.*, 2005, 4027–4030.

82 J. D. E. T. Wilton-Ely, D. Solanki, E. R. Knight, K. B. Holt, A. L. Thompson and G. Hogarth, Multimetallic assemblies using piperazine-based dithiocarbamate building blocks, *Inorg. Chem.*, 2008, **47**, 9642–9653.

83 E. R. Knight, N. H. Leung, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, Multimetallic Arrays: Bi-, Tri-, Tetra-, and Hexametallic Complexes Based on Gold(I) and Gold(III) and the Surface Functionalization of Gold Nanoparticles with Transition Metals, *Inorg. Chem.*, 2009, **48**, 3866–3874.

84 E. R. Knight, N. H. Leung, Y. H. Lin, A. R. Cowley, D. J. Watkin, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, Multimetallic arrays: symmetrical bi-, tri- and tetrametallic complexes based on the group 10 metals and the functionalization of gold nanoparticles with nickel-phosphine surface units, *Dalton Trans.*, 2009, 3688–3697.

85 K. Oliver, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, Multimetallic complexes of group 10 and 11 metals based on polydentate dithiocarbamate ligands, *Dalton Trans.*, 2011, **40**, 5852–5864.

86 M. J. Macgregor, G. Hogarth, A. L. Thompson and J. D. E. T. Wilton-Ely, Multimetallic Arrays: Symmetrical and Unsymmetrical Bi-, Tri-, and Tetrametallic Organometallic Complexes of Ruthenium(II) and Osmium (II), *Organometallics*, 2009, **28**, 197–208.

87 E. Humeres, N. A. Debacher, J. D. Franco, B. S. Lee and A. Martendal, Mechanisms of Acid Decomposition of Dithiocarbamates. 3. Aryldithiocarbamates and the Torsional Effect, *J. Org. Chem.*, 2002, **67**, 3662–3667.

88 S. C. Ball, I. Cragg-Hine, M. G. Davidson, R. P. Davies, A. J. Edwards, I. Lopez-Solera, P. R. Raithby and R. Snaith, Lithium intermediates during the α-lithiation and subsequent α-substitution of heterocyclic amines in the presence of CO_2, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 921–923.

89 P. Padungros and A. Wei, Practical Synthesis of Aromatic Dithiocarbamates, *Synth. Commun.*, 2014, **44**, 2336–2343.

90 M. Uchiyama, K. Satoh and M. Kamigaito, Cationic RAFT Polymerization Using ppm Concentrations of Organic Acid, *Angew. Chem., Int. Ed.*, 2015, **54**, 1924–1928.

91 H. Ma, G. Wang, G. T. Yee, J. L. Petersen and M. P. Jensen, Scorpionate-supported models of nickel-dependent superoxide dismutase, *Inorg. Chim. Acta*, 2009, **362**, 4563–4569.

92 B. Ballard, D. Wycoff, E. R. Birnbaum, K. D. John, J. W. Lenz, S. S. Jurisson, C. S. Cutler, F. M. Nortier, W. A. Taylor and M. E. Fassbender, Selenium-72 formation via $^{nat}Br(p,x)$ induced by 100 MeV Protons: Steps towards a novel $^{72}Se/^{72}As$ generator system, *Appl. Radiat. Isot.*, 2012, **70**, 595–601.

93 K. S. Siddiqi and N. Nishat, Synthesis and characterization of succinimide and phthalimide dithiocarbamates and their complexes with some transition metal ions, *Synth. React. Inorg. Met.-Org. Chem.*, 2000, **30**, 1505–1518.

94 I. F. Alshdoukhi, A. S. M. O. Al-Barwari, N. M. Aziz, T. Khalil, A. S. Faihan, S. A. Al-Jibori and A. S. Al-Janabi, Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) complexes of the newly prepared 1,2-benzoisothiazol-3(2H)-dithiocarbamate (BIT-DTC) ligand, *Bull. Chem. Soc. Ethiop.*, 2024, **38**, 889–899.

95 M. Y. Mohammed, Z. M. Mustafa and F. N. Aziz, Synthesis, Characterization, and Antibacterial Activity of Co(II), Ni(II), and Pd(II) Complexes with Bisdithiocarbamate and Cyclic Amines Ligands, *Macromol. Symp.*, 2022, **401**, 2100341.

96 M. Y. Mohammed, M. G. Abdel Karim and H. M. Abdul Karim, Synthesis, Characterization, and Bacterial Activity of Co(II), Ni(II), and Pd(II) Complexes with Ligands of Thymine, Uracil Thiuram Disulfur, and Cyclic Amines, *Macromol. Symp.*, 2022, **401**, 2100310.

97 H. W. Omar, M. Y. Mohammed and A. I. Yaseen, Synthesis and Characterization of Silver(I) Macromolecules Containing Macrocyclic Dithiocarbamate Ligand and Phosphines, *Macromol. Symp.*, 2025, **414**, 2400217.

98 T. Takeshima, M. Ikeda, M. Yokoyama, N. Fukada and M. Muraoka, Reaction of carbon disulfide with cyclic amides and related compounds. Free N-acyl- and N-carbamoyl-dithiocarbamic acids, *J. Chem. Soc., Perkin Trans. 1*, 1979, 692–695.

99 J. Chiefari, R. T. A. Mayadunne, C. L. Moad, G. Moad, E. Rizzardo, A. Postma, M. A. Skidmore and S. H. Thang, Thiocarbonylthio Compounds (S:C(Z)S-R) in Free Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (RAFT Polymerization). Effect of the Activating Group Z, *Macromolecules*, 2003, **36**, 2273–2283.

100 H. Aoshima, M. Uchiyama, K. Satoh and M. Kamigaito, Interconvertible Living Radical and Cationic Polymerization through Reversible Activation of Dormant Species with Dual Activity, *Angew. Chem., Int. Ed.*, 2014, **53**, 10932–10936.

101 R. Gerner, G. Kiel and G. Gattow, Chalcogenolates. 148. Reaction of formamide with carbon disulfide. 2. Crystal structure of potassium N-formyldithiocarbamate, *Z. Anorg. Allg. Chem.*, 1985, **523**, 76–88.

102 C. C. Hadjikostas and G. A. Katsoulos, Synthesis and characterization of 2-pyrrolidone-N-carbodithioato complexes of several transition metals, *Int. J. Chem.*, 1994, **5**, 49–57.

103 P. J. Heard, Y. S. Tan, C. I. Yeo and E. R. T. Tiekink, The Coordination Chemistry of Imidomethanedithiolate Dianions: A Structural Comparison with Their Dithiocarbamate Analogs, *Inorganics*, 2021, **9**, 71.

104 C. C. Hadjikostas, G. A. Katsoulos, M. P. Sigalas and C. A. Tsipis, Carbodithioato derivatives of weak nitrogen-

ous nucleophiles. II. Nondirect syntheses and structural studies of nickel(II) N-carbodithioates with substituted ureas, carbamic esters and sulfonamides, *Inorg. Chim. Acta*, 1989, **163**, 173–176.

105 C. C. Hadjikostas, G. A. Katsoulos, M. P. Sigalas and C. A. Tsipis, Carbodithioato derivatives of weak nitrogenous nucleophiles. I. Electronic structure and ground state properties of nickel(II) amide N-carbodithioates, *Can. J. Chem.*, 1989, **67**, 902–909.

106 C. C. Hadjikostas, G. A. Katsoulos, M. P. Sigalas, C. A. Tsipis and N. V. Duffy, Convenient, straightforward routes to carbodithioato derivatives of weak nitrogenous nucleophiles, *Polyhedron*, 1989, **8**, 2637–2639.

107 J. Salah, H. P. Bridges, D. Pugh and G. Hogarth, unpublished results.

108 B. Cvek, The Promiscuity of Disulfiram in Medicinal Research, *ACS Med. Chem. Lett.*, 2023, **14**, 1610–1614.

109 A. Bera, B. Busupalli and B. L. V. Prasad, Solvent-Less Solid State Synthesis of Dispersible Metal and Semiconducting Metal Sulfide Nanocrystals, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12006–12016.

110 A. Bera, D. Mandal, P. N. Goswami, A. K. Rath and B. L. V. Prasad, Generic and Scalable Method for the Preparation of Monodispersed Metal Sulfide Nanocrystals with Tuneable Optical Properties, *Langmuir*, 2018, **34**, 13459–13460.

111 A. Bera, B. Busupalli and B. L. V. Prasad, Solvent-Less Solid State Synthesis of Dispersible Metal and Semiconducting Metal Sulfide Nanocrystals, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12006–12016.

112 C. Jin, Y. Li, J. Lin, X. Guo, Y. Shi, H. Zhu, Y. Wang and X. Zhang, Efficient Transition Metal Sulfide Electrocatalysts Prepared by Laser-Induced Precursor Decomposition, *Appl. Energy Mater.*, 2024, **7**, 8546–8533.

113 S. J. Joris, K. I. Aspila and C. L. Chakrabarti, Monobasic or dibasic character of dithiocarbamic acids, *Anal. Chem.*, 1969, **41**, 1441–1445.

114 S. J. Joris, K. I. Aspila and C. L. Chakrabarti, On the Mechanism of Decomposition of Dithiocarbamates, *J. Phys. Chem.*, 1970, **74**, 860–865.

115 R. R. Vandebeek, S. J. Joris, K. I. Aspila and C. L. Chakrabarti, Decomposition of some cyclic dithiocarbamates, *Can. J. Chem.*, 1970, **48**, 2204–2209.

116 K. I. Aspila, S. J. Joris and C. L. Chakrabarti, Solvent Isotope Effects on Decomposition of N,N′-Dialkyldithiocarbamic Acids, *Anal. Chem.*, 1971, **43**, 1529–1530.

117 D. De Filippo, P. Deplano, F. Devillanova, E. F. Trogu and G. Verani, Inductive effect in dithiocarbamate decomposition mechanism, *J. Org. Chem.*, 1973, **38**, 560–563.

118 F. Takami, K. Tokuyama, S. Wakahara and T. Maeda, Decomposition of dithiocarbamates. VI. Decomposition of N-monosubstituted dithiocarbamic acids in acidic solutions, *Chem. Pharm. Bull.*, 1973, **21**, 594–599.

119 E. Humeres, N. A. Debacher, M. de Marta, J. D. Franco and A. Schutz, Mechanisms of Acid Decomposition of Dithiocarbamates. 1. Alkyl Dithiocarbamates, *J. Org. Chem.*, 1998, **63**, 1598–1603.

120 E. Humeres, N. A. Debacher and M. M. D. S. Sierra, Mechanisms of Acid Decomposition of Dithiocarbamates. 2. Efficiency of the Intramolecular General Acid Catalysis, *J. Org. Chem.*, 1999, **64**, 1807–1813.

121 E. Humeres, N. A. Debacher, J. D. Franco, B. S. Lee and A. Martendal, Mechanisms of Acid Decomposition of Dithiocarbamates. 3. Aryldithiocarbamates and the Torsional Effect, *J. Org. Chem.*, 2002, **67**, 3662–3667.

122 E. Humeres, B. S. Lee and N. A. Debacher, Mechanisms of Acid Decomposition of Dithiocarbamates. 5. Piperidyl Dithiocarbamate and Analogues, *J. Org. Chem.*, 2008, **73**, 7189–7196.

123 M. L. Riekkola and H. Siren, The rate of decomposition of sodium diisobutyldithiocarbamate in aqueous solution and extractability of the corresponding acid with methylene chloride, *Finn. Chem. Lett.*, 1983, 68–73.

124 V. Amarnath, K. Amarnath and W. M. Valentine, Mechanism of decomposition of N,N-dialkyl dithiocarbamates, *Curr. Top. Toxicol.*, 2007, **4**, 39–44.

125 A. W. DeMartino, M. L. Souza and P. C. Ford, Uncaging carbon disulfide. Delivery platforms for potential pharmacological applications: a mechanistic approach, *Chem. Sci.*, 2017, **8**, 7186–7196.

126 Y. Gao and B. Xia, Microdroplet accelerated reaction for high-efficiency carbon disulfide conversion, *Chem. Commun.*, 2023, **59**, 10773–10776.

127 B. Maeda and K. Murakami, Recent advancement in the synthesis of isothiocyanates, *Chem. Commun.*, 2024, **60**, 2839–2864.

128 R. Wong and S. J. Dolman, Isothiocyanates from Tosyl Chloride Mediated Decomposition of in Situ Generated Dithiocarbamic Acid Salts, *J. Org. Chem.*, 2007, **72**, 3969–3971.

129 S. Murru, H. Ghosh, S. K. Sahoo and B. K. Patel, Intra- and Intermolecular C-S Bond Formation Using a Single Catalytic System: First Direct Access to Arylthiobenzothiazoles, *Org. Lett.*, 2009, **11**, 4254–4257.

130 B. Luo, Q. Cui, H. Luo, Y. Hu, P. Huang and S. Wen, N-Benzyldithiocarbamate Salts as Sulfur Sources to Access Tricyclic Thioheterocycles Mediated by Copper Species, *Adv. Synth. Catal.*, 2016, **358**, 2733–2738.

131 A. Z. Halimehjani, S. Shokrgozar and P. Beier, Transition-Metal-Free Coupling Reaction of Dithiocarbamates with Indoles: C-S Bond Formation, *J. Org. Chem.*, 2018, **83**, 5778–5783.

132 J. Nath, H. Ghosh, R. Yella and B. K. Patel, Molecular Iodine Mediated Preparation of Isothiocyanates from Dithiocarbamic Acid Salts, *Eur. J. Org. Chem.*, 2009, 1849–1851.

133 J. Nath, P. Jamir and B. K. Patel, Improved procedure for the preparation of isothiocyanates via iodine-mediated desulfurization of dithiocarbamic acid salts, *Green Chem. Lett. Rev.*, 2011, **4**, 1–34.

134 H. C. Brinkhoff, J. A. Cras, J. J. Steggerda and J. Willemse, Oxidation of dithiocarbamate complexes of nickel,

copper, and zinc, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 633–640.

135 S. Thirumaran, K. Ramalingam, G. Bocelli and A. Cantoni, Spectral and single crystal X-ray structural studies on disulfide complexes: reaction of bis(dialkyldithiocarbamato)M(II) with iodine and crystal structure determination of diiodo(bipiperidinethiuramdisulfide)M(II) (M = zinc, cadmium), *Polyhedron*, 2000, **19**, 1279–1282.

136 F. Liang, J. Tan, C. Piao and Q. Liu, Carbon tetrabromide promoted reaction of amines with carbon disulfide: facile and efficient synthesis of thioureas and thiuram disulfides, *Synthesis*, 2008, 3579–3584.

137 S. Techapanalai, R. M. Annuur, M. Sukwattanasinitt and S. Wach, arasindhu, One-Pot Synthesis of Isothiocyanates from Amines Mediated by Carbon Tetrabromide, *ChemistrySelect*, 2023, **8**, e202302045.

138 Z. Fu, W. Yuan, N. Chen, Z. Yang and J. Xu, $Na_2S_2O_8$-mediated efficient synthesis of isothiocyanates from primary amines in water, *Green Chem.*, 2018, **20**, 4484–4491.

139 D. Li, Y. Shu, P. Li, W. Zhang, H. Ni and Y. Cao, Synthesis and structure-activity relationships of aliphatic isothiocyanate analogs as antibiotic agents, *Med. Chem. Res.*, 2013, **22**, 3119–3125.

140 J. Ma, F. Li, C. Wang, Z. Wang, C. Du and L. Wang, Synthesis of Isothiocyanates from Primary Amines via Visible-Light Photocatalysis, *Org. Lett.*, 2023, **25**, 5692–5696.

141 There were 3749 hits in the CSD version 5.45 (November 2023) for metal dithiocarbamate complexes.

142 D. V. Konarev, A. Y. Kovalevsky, S. S. Khasanov, G. Saito, D. V. Lopatin, A. V. Umrikhin, A. Otsuka and R. N. Lyubovskaya, Synthesis, crystal structures, magnetic properties and photoconductivity of C_{60} and C_{70} complexes with metal dialkyldithiocarbamates $M(R_2dtc)_x$, where M = CuII, CuI, AgI, ZnII, CdII, HgII, MnII, NiII, and PtII; R = Me, Et, and nPr, *Eur. J. Inorg. Chem.*, 2006, 1881–1895.

143 D. V. Konarev, S. S. Khasanov, D. V. Lopatin, V. V. Rodaev and R. N. Lyubovskaya, Fullerene complexes with divalent metal dithiocarbamates: structures, magnetic properties, and photoconductivity, *Russ. Chem. Bull.*, 2007, **56**, 2145–2161.

144 D. V. Konarev, S. S. Khasanov, A. Y. Kovalevsky, D. V. Lopatin, V. V. Rodaev, G. Saito, B. Nara, L. Forro and R. N. Lyubovskaya, Supramolecular approach to the synthesis of [60]fullerene-metal dithiocarbamate complexes, $\{(MII(R_2dtc)_2)_x{\cdot}L\}{\cdot}C_{60}$ (M = Zn, Cd, Hg, Fe, and Mn; x = 1 and 2). The study of magnetic properties and photoconductivity, *Cryst. Growth Des.*, 2008, **8**, 1161–1172.

145 E. C. Alyea, D. C. Bradley, M. F. Lappert and A. R. Sanger, Lower valent dialkylamides of titanium and vanadium, *J. Chem. Soc., Chem. Commun.*, 1969, 1064–1065.

146 D. C. Bradley and M. H. Gitlitz, Preparation and Properties of N,N-Dialkyldithiocarbamates of Early Transition Elements, *J. Chem. Soc. A*, 1969, 1152–1156.

147 A. C. Behrle, A. J. Myers, A. Kerridge and J. R. Walensky, Coordination Chemistry and QTAIM Analysis of Homoleptic Dithiocarbamate Complexes, $M(S_2CN^iPr_2)_4$ (M = Ti, Zr, Hf, Th, U, Np), *Inorg. Chem.*, 2018, **57**, 10518–10524.

148 M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse and I. F. Rendall, Structural studies of metal dithiocarbamates. VI. Crystal and molecular structure of tetrakis(N,N-diethyldithiocarbamato)titanium(IV), *J. Chem. Soc., Dalton Trans.*, 1972, 1052–1057.

149 G. L. Campbell, G. D. Ellis and M. R. Chakrabarty, The synthesis and characterization of some titanium(III) tris-N,N-dialkyldithiocarbamates, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2265–2268.

150 R. E. Jilek, G. Tripepi, E. Urnezius, W. W. Brennessel, V. G. Young Jr. and J. E. Ellis, Zerovalent titanium-sulfur complexes. Novel dithiocarbamato derivatives of $Ti(CO)_6$: $[Ti(CO)_4(S_2CNR_2)]^-$, *Chem. Commun.*, 2007, 2639–2641.

151 L. F. Larkworthy and M. W. O'Donoghue, Synthesis and properties of vanadium(III) dithiocarbamates, *Inorg. Chim. Acta*, 1983, **74**, 155–158.

152 H. P. Zhu, Y.-H. Deng, X.-Y. Huang, C.-N. Chen and Q.-T. Liu, Tris(N,N-diethyldithiocarbamato-S,S')vanadium(III), *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 692–693.

153 S. Sproules, T. Weyhermueller, S. De Beer and K. Wieghardt, Six-Membered Electron Transfer Series $[V(dithiolene)_3]z$ (z = 1+, 0, 1-, 2-, 3-, 4-). An X-ray Absorption Spectroscopic and Density Functional Theoretical Study, *Inorg. Chem.*, 2010, **49**, 5241–5261.

154 T. L. Riechel, L. J. De Hayes and D. T. Sawyer, Electrochemical studies of vanadium(III), -(IV), and -(V) complexes of diethyldithiocarbamate in acetonitrile, *Inorg. Chem.*, 1976, **15**, 1900–1904.

155 D. C. Bradley, I. F. Rendall and K. D. Sales, Covalent compounds of quadrivalent transition metals. VI. Spectroscopic studies on titanium, vanadium, and zirconium diethyldithiocarbamates, *J. Chem. Soc., Dalton Trans.*, 1973, 2228–2233.

156 B. J. McCormick, Structure and spectra of dithiocarbamate complexes of oxovanadium(IV), *Inorg. Chem.*, 1968, **7**, 1965–1970.

157 H. Sakurai, H. Watanabe, H. Tamura, H. Yasui, R. Matsushita and J. Takada, Insulin-mimetic vanadyl-dithiocarbamate complexes, *Inorg. Chim. Acta*, 1998, **283**, 175–183.

158 M. Atzori, L. Tesi, S. Benci, A. Lunghi, R. Righini, A. Taschin, R. Torre, L. Sorace and R. Sessoli, Spin Dynamics and Low Energy Vibrations: Insights from Vanadyl-Based Potential Molecular Qubits, *J. Am. Chem. Soc.*, 2017, **139**, 4338–4341.

159 R. M. Golding, P. C. Healy, P. Colombera and A. H. White, NMR studies of some chromium(III) dithicarbamate complexes, *Aust. J. Chem.*, 1974, **27**, 2089–2097.

160 C. L. Raston and A. H. White, Crystal structure of tris(N,N-diethyldithiocarbamato) chromium(III), *Aust. J. Chem.*, 1977, **30**, 2091–2094.

161 D. J. Lewis, A. A. Tedstone, X. L. Zhong, E. A. Lewis, A. Rooney, N. Savjani, J. R. Brent, S. J. Haigh, M. G. Burke, C. A. Muryn, *et al.*, Thin Films of Molybdenum Disulfide Doped with Chromium by Aerosol-Assisted Chemical Vapor Deposition (AACVD), *Chem. Mater.*, 2015, **27**, 1367–1374.
162 J. P. Fackler Jr. and D. G. Holah, Sulfur chelates. II. Five-coordinate transition metal complexes, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 251–255.
163 R. Lancashire and T. D. Smith, Syntheses of diethyldithiocarbamate chelates of chromium(III) and molybdenum(V) by oxidative decarbonylation, *J. Chem. Soc., Dalton Trans.*, 1982, 845–846.
164 A. M. Bond and G. G. Wallace, Influence of oxygen insertion on the electrochemistry of chromium(III) dithiocarbamate complexes, *Inorg. Chem.*, 1984, **23**, 1858–1865.
165 L. Y. Goh, Z. Weng, W. K. Leong and P. H. Leung, C-S bond cleavage and C-C coupling in cyclopentadienylchromium complexes to give the first dithiooxamide-bridged and doubly dithiocarbamate-bridged double cubanes: $[Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}]$ and $[Cp_6Cr_8S_8(S_2CNEt_2)_2]$, *Angew. Chem., Int. Ed.*, 2001, **40**, 3236–3239.
166 G.-Y. He, F.-L. Bei, H.-Q. Chen and X.-Q. Sun, Solid-phase synthesis, crystal structure, and quantum chemical calculation of a molybdenum(II) complex with bis(diethyldithiocarbamate), *J. Chem. Crystallogr.*, 2006, **36**, 481–486.
167 R. Selvaraju, K. Panchanatheswaren, A. Thiruvalluvar and V. Parthasarathi, Redetermination of Bis(N,N-diethyldithiocarbamato)nickel(II), *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 606–608.
168 P. Vella and J. Zubieta, Preparation, characterization and electrochemical investigation of dimeric molybdenum thioxanthate complexes, $Mo_2(S_2CSR)_4$, and their relationship to analogous binuclear dithioacid complexes, *J. Inorg. Nucl. Chem.*, 1978, **40**, 477–487.
169 L. Ricard, J. Estienne and R. Weiss, Formation of a thiocarboxamidomolybdenum complex by oxidative bond cleavage. Crystal and molecular structure of bis[μ-sulfido-thiocarboxamido(dipropyldithiocarbamato)molybdenum], *Inorg. Chem.*, 1973, **12**, 2182–2186.
170 J. A. Broomhead and C. G. Young, Tungsten carbonyl complexes with dithiocarbamate ligands, *Aust. J. Chem.*, 1982, **35**, 277–285.
171 S. J. N. Burgmayer and J. L. Templeton, Synthesis and structure of a seven-coordinate molybdenum carbonyl fluoride derivative: $[Et_4N][Mo(CO)_2(S_2CNEt_2)_2F]$, *Inorg. Chem.*, 1985, **24**, 2224–2230.
172 D. M. Hill, L. F. Larkworthy and M. W. O'Donoghue, Manganese(II) compounds of N,N-disubstituted dithiocarbamates, *J. Chem. Soc., Dalton Trans.*, 1975, 1726–1728.
173 G. Reale, F. Calderoni, T. Ghirardi, F. Porto, F. Illuminati, L. Marvelli, P. Martini, L. Uccelli, E. Tonini, L. Del Bianco, F. Spizzo, M. Capozza, E. Cazzola, A. Carnevale, M. Giganti, A. Turra, J. Esposito and A. Boschi, Development and Evaluation of the Magnetic Properties of a New Manganese(II) Complex: A Potential MRI Contrast Agent, *Int. J. Mol. Sci.*, 2023, **24**, 3461.
174 M. Ciampolini, C. Mengozzi and P. Orioli, Structure and magnetic properties of bis(diethyldithiocarbamato) manganese(II), *J. Chem. Soc., Dalton Trans.*, 1975, 2051–2054.
175 P. Martini, A. Boschi, L. Marvelli, L. Uccelli, S. Carli, G. Cruciani, E. Marzola, A. Fantinati, J. Esposito and A. Duatti, Synthesis and Characterization of Manganese Dithiocarbamate Complexes: New Evidence of Dioxygen Activation, *Molecules*, 2021, **26**, 5954.
176 J. Qu, A. Elgendy, R. Cai, M. A. Buckingham, A. A. Papaderakis, H. de Latour, K. Hazeldine, G. F. S. Whitehead, F. Alam, C. T. Smith, D. J. Binks, A. Walton, J. M. Skelton, R. A. W. Dryfe, S. J. Haigh and D. J. Lewis, A Low-Temperature Synthetic Route Toward a High-Entropy 2D Hexernary Transition Metal Dichalcogenide for Hydrogen Evolution Electrocatalysis, *Adv. Sci.*, 2023, **10**, 2204488.
177 Y.-W. Jun, Y.-Y. Jung and J. Cheon, Architectural Control of Magnetic Semiconductor Nanocrystals, *J. Am. Chem. Soc.*, 2002, **124**, 615–619.
178 Y. Yang, O. Chen, A. Angerhofer and C. Y. Cao, Radial-Position-Controlled Doping in CdS/ZnS Core/Shell Nanocrystals, *J. Am. Chem. Soc.*, 2006, **128**, 12428–12429.
179 Y. Zhang, R. Xu, W. Chen, O. Zhuo, Q. Wu, J. Cai, X. Wang and Z. Hu, Solution-solid-solid growth of metastable wurtzite γ-MnS nanowires with controlled length, *J. Mater. Chem. C*, 2017, **5**, 6493–6496.
180 Y. Zhang, Y. Xue, K. Qi, Z. Ru, J. Cai and W. Chen, Construction of Various One-Dimensional ZnS/MnS Hetero-nanostructures with Varied Diameters via the Multistep Solution-Solid-Solid Growth Method, *Inorg. Chem.*, 2022, **61**, 1152–1158.
181 H. B. Ferraz, P. H. Bertolucci, J. S. Pereira, J. G. Lima and L. A. Andrade, Chronic exposure to the fungicide maneb may produce symptoms and signs of CNS manganese intoxication, *Neurology*, 1988, **38**, 550–553.
182 S. Costello, M. Cockburn, J. Bronstein, X. Zhang and B. Ritz, Parkinson's disease and residential exposure to maneb and paraquat from agricultural applications in the central valley of California, *Am. J. Epidemiol.*, 2009, **169**, 919–926.
183 L. Kubens, K.-N. Truong, C. W. Lehmann, D. Luetzenkirchen-Hecht, J. Bornhorst and F. Mohr, The Structure of Maneb, An Important Manganese-Containing Bis(dithiocarbamate) Fungicide, *Chem. – Eur. J.*, 2023, **29**, e202301721.
184 J. G. Lozano, F. Dillon, A. J. Naylor, L. Y. Lee, C. Lippard, D. Johnstone, P. G. Bruce and N. Grobert, Single Source Precursor Route to Iron Sulfide Nanomaterials for Energy Storage, *Chem. Phys. Lett.*, 2020, **739**, 136993.
185 O. A. Ileperuma and R. D. Feltham, Crystal and molecular structure of iron(II) bis(diethyldithiocarbamate), *Inorg. Chem.*, 1975, **14**, 3042–3045.
186 J. Lu, C.-H. Lu, J.-H. Yu, J.-Q. Xu, Y. Li, X. Zhang, T.-G. Wang and Q.-X. Yang, Syntheses, structures and third-order nonlinear optical properties of heterometal

and homometal clusters containing iron, *Polyhedron*, 2004, **23**, 755–761.

187 L. F. Larkworthy, B. W. Fitzsimmons and R. R. Patel, Magnetic and Mossbauer investigation of N,N-disubstituted(dithiocarbamato)-iron(II) complexes, *J. Chem. Soc., Chem. Commun.*, 1973, 902–903.

188 B. W. Fitzsimmons, S. E. Al-Mukhtar, L. F. Larkworthy and R. R. Patel, Magnetic and Mössbauer investigations of N,N-disubstituted bis(dithiocarbamato)iron(II) complexes, *J. Chem. Soc., Dalton Trans.*, 1975, 1969–1973.

189 R. H. Holm, L. H. Pinolet and R. A. Lewis, Synthesis and stereochemical rearrangements of complexes containing the Fe-S6 core, *J. Am. Chem. Soc.*, 1971, **93**, 360–371.

190 J. L. K. F. De Vries, J. M. Trooster and E. De Boer, Iron(II) complexes with two and three dialkyldithiocarbamate ligands. Mössbauer and electronic spectra, *Inorg. Chem.*, 1973, **12**, 2730–2733.

191 Y. Deng, T. Wen, Q. Liu, H. Zhu, C. Chen and D. Wu, Structure and characterization of a mononuclear FeII dialkyldithiocarbamate complex $Fe(OC_4H_8dtc)_2(DMF)$, *Inorg. Chim. Acta*, 1999, **293**, 95–99.

192 M. R. Houchin, Reactions of carbon monoxide with iron (II) diethyldithiocarbamate and iron(II) ethylxanthate, *Inorg. Chim. Acta*, 1984, **83**, 103–110.

193 G. Hogarth, N. Hollingsworth, H. Islam, W. Bras, N. H. De Leeuw, A. Roffey and G. Sankar, Fe(II) and Fe(III) dithiocarbamate complexes as single source precursors to nanoscale iron sulfides: A combined synthetic and *in situ* XAS approach, *Nanoscale Adv.*, 2019, **1**, 2965–2978.

194 G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais and P. G. Owston, Crystal and molecular structure of bis-(N,N-dimethyldithiocarbamato)-nitrosyliron (at −80 deg.), *J. Chem. Soc. A*, 1970, 1275–1283.

195 O. A. Ileperuma and R. D. Feltham, Iron-sulfur complexes of nitric oxide. 2. Synthesis and exchange studies of Fe $(NO)X[S_2CN(CH_3)_2]_2$. Crystal and molecular structure of cis-bis(diethyldithiocarbamato)(nitro)nitrosyliron, *Inorg. Chem.*, 1977, **16**, 1876–1883.

196 P. Mordvintcev, A. Muelsch, R. Busse and A. Vanin, On-line detection of nitric oxide formation in liquid aqueous phase by electron paramagnetic resonance spectroscopy, *Anal. Biochem.*, 1991, **199**, 142–146.

197 C. Csonka, T. Pali, P. Bencsik, A. Goerbe, P. Ferdinandy and T. Csont, Measurement of NO in biological samples, *Br. J. Pharmacol.*, 2015, **172**, 1620–1632.

198 S. Fujii and T. Yoshimura, A new trend in iron-dithiocarbamate complexes: as an endogenous NO trapping agent, *Coord. Chem. Rev.*, 2000, **198**, 89–99.

199 H. Kunkely and A. Vogler, Photochemistry of tris(diethyldithiocarbamato)iron(III). Reduction to a stable iron(II) complex induced by ligand-to-metal charge transfer excitation, *Inorg. Chem. Commun.*, 2002, **5**, 730–732.

200 W.-H. Leung, J. L. C. Chim, H. Hou, T. S. M. Hun, I. D. Williams and W.-T. Wong, Oxidation Reactions of Dithiocarbamate Complexes of Ruthenium(II), *Inorg. Chem.*, 1997, **36**, 4432–4437.

201 M. Md. Karim, N. Md. Abser, M. R. Hassan, N. Ghosh, H. G. Alt, I. Richards and G. Hogarth, Oxidative-addition of thiuram disulfides to osmium(0): Synthesis of cis-$[Os(CO)_2(S_2CNR_2)_2]$ (R = Me, Et, Cy, CH_2CH_2OMe) and molecular structures of cis-$[Os(CO)_2(S_2CNMe_2)_2]$ and $[(MeOCH_2CH_2)_2NCS]_2$, *Polyhedron*, 2012, **42**, 84–88.

202 Md. N. Huda, J. C. Sarker, V. N. Nesterov, G. Hogarth and S. E. Kabir, Oxidative-addition of tetramethylthiram disulfide (Me_4TDS) and monosulfide (Me_4TMS) at a triosmium centre: Generation of dithiocarbamate, trithiocarbamate, thiocarboxamide and amino-carbyne ligands, *J. Organomet. Chem.*, 2024, **1016**, 123252.

203 N. C. Bhoumik, Md. N. Huda, V. N. Nesterov, G. Hogarth, S. E. Kabir and J. C. Sarker, Reactivity of Labile Triosmium Complexes, $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with Tetraethylthiuram Disulfide (Disulfiram), *J. Cluster Sci.*, 2025, **36**, 34.

204 R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn and A. H. White, Temperature dependence of the proton nuclear magnetic resonance spectra of some diamagnetic N,N-dialkyldithiocarbamate complexes of transition metals, *Inorg. Chem.*, 1972, **11**, 2435–2440.

205 P. C. Healy, J. W. Connor, B. W. Skelton and A. H. White, Alkyl substituent effects in diamagnetic dithiocarbamate cobalt(III) and nickel(II) complexes, *Aust. J. Chem.*, 1990, **43**, 1083–1095.

206 F. Jian, F. Bei, P. Zhao, X. Wang, H. Fun and K. Chinnakali, Synthesis, crystal structure and stability studies of dithiocarbamate complexes of some transition elements (M = Co, Ni, Pd), *J. Coord. Chem.*, 2002, **55**, 429–437.

207 N. V. Khitrich, V. G. Vlasenko, I. I. Seifullina, Ya. V. Zubavichus, S. I. Levchenkov and L. S. Skorokhod, Local surrounding of cobalt(II) in dithiocarbamate complexes, their magnetic and spectral properties, *Russ. J. Gen. Chem.*, 2014, **84**, 555–561.

208 A. M. Bond, A. R. Hendrickson, R. L. Martin, J. E. Moir and D. R. Page, Electrochemical reduction and oxidation of cobalt(III) dithiocarbamates, *Inorg. Chem.*, 1983, **22**, 3440–3446.

209 G. Hogarth, K. T. Holman, A. Pateman, A. Sella, J. W. Steed and I. Richards, Multiple nitrene insertions into metal-sulfur bonds of dithiocarbamate complexes: synthesis of sulfido-amido and zwitterionic tetraamido complexes, *Dalton Trans.*, 2005, 2688–2695.

210 K. K. Pandey, D. T. Nehete and R. B. Sharma, Square planar and square pyramidal complexes of rhodium(II), *Polyhedron*, 1990, **9**, 2013–2018.

211 N. M. Sosibo and N. Revaprasadu, Synthesis and characterization of rhodium sulfide nanoparticles and thin films, *Mater. Sci. Eng., B*, 2008, **150**, 111–115.

212 C. L. Raston and A. H. White, Crystal structures of tris(diethyldithiocarbamato)rhodium(III) and -arsenic(III), *J. Chem. Soc., Dalton Trans.*, 1975, 2425–2429.

213 C. G. Sceney and R. J. Magee, Iridium(III) dithiocarbamate complexes, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 595–597.

214 A. M. Bond, R. Colton and D. R. Mann, Electrochemical investigation of kinetic and thermodynamic aspects of oxidation and reduction of mononuclear and binuclear rhodium dithiocarbamate and diselenocarbamate complexes, *Inorg. Chem.*, 1989, **28**, 54–59.

215 S. Lahiry and V. K. Anand, Manganese(II) complex in a pure spin quartet state, *J. Chem. Soc., Chem. Commun.*, 1971, 1111–1112.

216 S. Tellez, C. A. Costa Jr., M. A. Mondragon, G. B. Ferreira, O. Versiane, J. L. Rangel, G. Lima and M. A. A. Muller, Molecular structure, natural bond analysis, vibrational and electronic spectra, surface enhanced Raman scattering and Mulliken atomic charges of the normal modes of [Mn(DDTC)$_2$] complex, *Spectrochim. Acta, Part A*, 2016, **169**, 95–107.

217 C. A. T. Zepeda, A. Coelho, O. Versiane, M. A. Mondragon, R. S. Pessoa and C. A. Téllez Soto, Synthesis, structure determination, NBO analysis and vibrational/electronic spectroscopic study of Iron(II) Bis(diethyldithiocarbamate) [Fe(DDTC)$_2$], *J. Mol. Struct.*, 2023, **1287**, 135618.

218 A. C. Costa Jr., O. Versiane, O. G. Faget, J. M. Ramos, G. B. Ferreira, A. A. Martin and C. A. Téllez Soto, An experimental and theoretical approach of spectroscopic and structural properties of the bis(diethyldithiocarbamate)-cobalt(II), *J. Mol. Struct.*, 2012, **1029**, 119–134.

219 R. R. Eley, R. R. Myers and N. V. Duffy, Electron spin crossover in iron(III) dithiocarbamates, *Inorg. Chem.*, 1972, **11**, 1128–1130.

220 H. L. Nigam, K. B. Pandeya and R. Singh, $^6A_{1g}\rightleftharpoons{}^2T_{2g}$ spin-crossover in iron(III) dithiocarbamates, *J. Indian Chem. Soc.*, 2001, **78**, 525–532.

221 A. H. Ewald, R. L. Martin, E. Sinn and A. H. White, Electronic equilibrium between the $6A^1$ and $2T^2$ states in iron(III) dithio chelates, *Inorg. Chem.*, 1969, **8**, 1837–1846.

222 C. Milsmann, S. Sproules, E. Bill, T. Weyhermueller, S. D. George and K. Wieghardt, Stabilization of High-Valent FeIVS$_6$-Cores by Dithiocarbamate(1-) and 1,2-Dithiolate(2-) Ligands in Octahedral [FeIV(Et$_2$dtc)$_{3(-n}$(mnt)$_n$]$^{(n-1)-}$ Complexes (n = 0, 1, 2, 3): A Spectroscopic and Density Functional Theory Computational Study, *Chem. – Eur. J.*, 2010, **16**, 3628–3645.

223 L. H. Pignolet, Dynamic stereochemistry of tris-chelate complexes. IV. Crystal structure of tris(N,N-diethyldithiocarbamato)ruthenium(III), *Inorg. Chem.*, 1974, **13**, 2051–2055.

224 R. E. DeSimone, Electron paramagnetic resonance studies of low-spin d5 complexes. Trisbidentate complexes of iron (III), ruthenium(III), and osmium(III) with sulfur-donor ligands, *J. Am. Chem. Soc.*, 1973, **95**, 6238–6244.

225 G. R. Hall and D. N. Hendrickson, Ferric tris(dithiocarbamate) spin equilibrium revisited. Variable-temperature (4.2–296 deg K) magnetic susceptibility, (30–300 deg K) infrared, and (4.2–85 deg K) electron paramagnetic resonance data, *Inorg. Chem.*, 1976, **15**, 607–618.

226 A. M. Paca, M. Singh and P. A. Ajibade, Synthesis, characterization and in vitro anticancer studies of Ru(III) dithiocarbamate complexes, *J. Coord. Chem.*, 2022, **75**, 2923–2932.

227 J. Z. Mbese and P. A. Ajibade, Synthesis, spectroscopic, structural and optical studies of Ru_2S_3 nanoparticles prepared from single-source molecular precursors, *J. Mol. Struct.*, 2017, **1143**, 274–281.

228 J. Z. Mbese and P. A. Ajibade, Homonuclear tris-dithiocarbamato ruthenium(III) complexes as single-molecule precursors for the synthesis of ruthenium(III) sulfide nanoparticles, *J. Sulfur Chem.*, 2017, **38**, 173–187.

229 L. Giovagnini, S. Sitran, I. Castagliuolo, P. Brun, M. Corsini, P. Zanello, A. Zoleo, A. Maniero, B. Biondi and D. Fregona, Ru(III)-based compounds with sulfur donor ligands: synthesis, characterization, electrochemical behaviour and anticancer activity, *Dalton Trans.*, 2008, 6699–6708.

230 E. M. Nagy, C. Nardon, L. Giovagnini, L. Marchio, A. Trevisan and D. Fregona, Promising anticancer mono- and dinuclear ruthenium(III) dithiocarbamato complexes: systematic solution studies, *Dalton Trans.*, 2011, **40**, 11885–11895.

231 L. Brustolin, C. Nardon, N. Pettenuzzo, N. Zuin Fantoni, S. Quarta, F. Chiara, A. Gambalunga, A. Trevisan, L. Marchio, P. Pontisso, *et al.*, Synthesis, chemical characterization and cancer cell growth-inhibitory activities of Cu(II) and Ru(III) aliphatic and aromatic dithiocarbamato complexes, *Dalton Trans.*, 2018, **47**, 15477–15486.

232 A. R. Hendrickson, J. M. Hope and R. L. Martin, Tris- and pentakis-dialkyldithiocarbamates of ruthenium, [Ru(S$_2$CNR$_2$)$_3$]$_n$ and [Ru$_2$(S$_2$CNR$_2$)$_5$]$_n$ (n = +1, 0, and −1): chemical and electrochemical interrelations, *J. Chem. Soc., Dalton Trans.*, 1976, 2032.

233 K. W. Given, S. H. Wheeler, B. S. Jick, L. J. Maheu and L. H. Pignolet, Synthesis, characterization, and electrochemical properties of dithiocarbamato complexes of osmium(III) and -(IV), *Inorg. Chem.*, 1979, **18**, 1261–1266.

234 E. R. T. Tiekink and I. Haiduc, Stereochemical aspects of metal xanthate complexes: Molecular structures and supramolecular self-assembly, *Prog. Inorg. Chem.*, 2005, **54**, 127–319.

235 P. J. Heard, K. Kite, J. S. Nielsen and D. A. Tocher, Trimethylplatinum(IV) complexes of dithiocarbamato ligands: an experimental NMR study on the barrier to C-N bond rotation, *Dalton Trans.*, 2000, 1349–1356.

236 M. Moriyasu, Y. Hashimoto and M. Endo, Kinetic studies of fast equilibrium by means of high-performance liquid chromatography. IV. Separation of rotamers of palladium (II) dithiocarbamates, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1972–1977.

237 W. H. Pan, T. R. Halbert, L. L. Hutchings and E. I. Stiefel, Ligand and induced internal electron transfer pathways to new molybdenum-sulfur and tungsten-sulfur dithiocarbamate complexes, *J. Chem. Soc., Chem. Commun.*, 1985, 927–929.

238 M. A. Harmer, T. R. Halbert, W. H. Pan, C. L. Coyle, S. A. Cohen and E. I. Stiefel, Ligand and induced internal redox processes in molybdenum- and tungsten-sulfur systems, *Polyhedron*, 1986, **5**, 341–347.
239 T. R. Halbert, L. L. Hutchings, R. Rhodes and E. I. Stiefel, Induced redox reactivity of tetrathiovanadate(V): synthesis of the vanadium(IV) dimer $V_2(\mu\text{-}S_2)_2(\text{iso-}Bu_2NCS_2)_4$ and its structural relationship to the V/S mineral patronite, *J. Am. Chem. Soc.*, 1986, **108**, 6437–6438.
240 L. Wei, T. R. Halbert, H. H. Murray III and E. I. Stiefel, Induced internal electron transfer reactivity of tetrathioperrhenate(VII): synthesis of the interconvertible dimers $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ and $[Re_2(\mu\text{-}SS_2CNR_2)_2(S_2CNR_2)_3][O_3SCF_3]$ (R = Me, iso-Bu), *J. Am. Chem. Soc.*, 1990, **112**, 6431–6433.
241 Y. Gea, M. A. Greaney, C. I. Coyle and E. I. Stiefel, Analogous reactivity of MoS_4^{2-} and WSe_4^{2}: preparation of $WSe_2(\text{iso-}Bu_2NCS_2)_3$ by an induced internal redox reaction, *J. Chem. Soc., Chem. Commun.*, 1992, 160–161.
242 J. M. Hope, R. L. Martin, D. Taylor and A. H. White, Ring expansion in a metal-dithiocarbamate complex by oxygen insertion; synthesis and properties of $[Cr(S_2CNR_2)_2(OS_2CNR_2)]$. The X-ray structure of bis[NN-diethyl(dithiocarbamato-SS')][NN-diethyl(dithioperoxycarbamato-OS)]chromium(III), *J. Chem. Soc., Chem. Commun.*, 1977, 99–100.
243 S. Ng, J. W. Ziller and P. J. Farmer, Multiple Pathways for the Oxygenation of a Ruthenium(II) Dithiocarbamate Complex: S-Oxygenation and S-Extrusion, *Inorg. Chem.*, 2004, **43**, 8301–8309.
244 D. F. Brayton, K. Tanabe, M. Khiterer, K. Kolahi, J. Ziller, J. Greaves and P. J. Farmer, Oxygenation of Zinc Dialkyldithiocarbamate Complexes: Isolation, Characterization, and Reactivity of the Stoichiometric Oxygenates, *Inorg. Chem.*, 2006, **45**, 6064–6072.
245 E. Eijarvi, L. H. J. Lajunen and M. Heikka, Simultaneous determination of chromium(III) and chromium(VI) by reversed-phase high performance liquid chromatography with UV detection, *Finn. Chem. Lett.*, 1985, 225–230.
246 Y. Honma, Formation of two chromium(III) dithiocarbamates from Cr(VI) in solvent extraction system and origin of oxygen atom in bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio (thioperoxoato)]chromium(III), *Bull. Chem. Soc. Jpn.*, 2002, **75**, 2415–2421.
247 M. Safari, S. Nojavan, S. S. H. Davarani and A. Morteza-Najarian, Speciation of chromium in environmental samples by dual electromembrane extraction system followed by high performance liquid chromatography, *Anal. Chim. Acta*, 2013, **789**, 58–64.
248 L. F. Shvydka, Yu. I. Usatenko and F. M. Tulyupa, Strength of osmium(VI) dithiocarbamates, *Zh. Neorg. Khim.*, 1973, **18**, 756–761.
249 W. P. Griffith and J. M. Jolliffe, Studies on transition-metal nitrido and oxo complexes. Part 14. Carboxylato oxo-osmium(VI) and -ruthenium(VI) complexes and their reactions, *J. Chem. Soc., Dalton Trans.*, 1992, 3483–3488.
250 C. Nardon, S. M. Schmitt, H. Yang, J. Zuo, D. Fregona and Q. P. Dou, Gold(III)-Dithiocarbamato Peptidomimetics in the Forefront of the Targeted Anticancer Therapy: Preclinical Studies against Human Breast Neoplasia, *PLoS One*, 2014, **9**, e84248.
251 H. J. A. Blaauw, R. J. F. Nivard and G. J. M. van der Kerk, Chemistry of organogold compounds: I. Syntheses and properties of dihalogold(III) *N*,*N*-dialkyldithiocarbamates and dialkylgold(III) *N*,*N*-dialkyldithiocarbamates, *J. Organomet. Chem.*, 1964, **2**, 236–244.
252 R. K. Brown, J. N. Bunyan, A. Agrawal, G. Li, D. Dautoras, J. C. Sarker, T. T. Keat, T. Hicks, G. Hogarth and D. Pugh, A Revised Understanding of the Speciation of Gold(III) Dithiocarbamate Complexes in Solution, *Dalton Trans.*, 2025, **54**, 7627–7640.
253 J. Cordón, G. Jiménez-Osés, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and D. Pascual, Experimental and Theoretical Study of Gold(III)-Catalyzed Hydration of Alkynes, *Organometallics*, 2014, **33**, 3823–3830.
254 L. Giovagnini, L. Ronconi, D. Aldinucci, D. Lorenzon, S. Sitran and D. Fregona, Synthesis, Characterization, and Comparative in Vitro Cytotoxicity Studies of Platinum(II), Palladium(II), and Gold(III) Methylsarcosinedithiocarbamate Complexes, *J. Med. Chem.*, 2005, **48**, 1588–1595.
255 M. Altaf, A. A. Isab, J. Vančo, Z. Dvorák, Z. Trávníček and H. Stoeckli-Evans, Synthesis, characterization and *in vitro* cytotoxicity of gold(III) dialkyl/diaryldithiocarbamato complexes, *RSC Adv.*, 2015, **5**, 81599–81607.
256 O. Loseva, Private communication to the CCDC, deposition number 1977816.
257 A. Angeloski, K. Flower-Donaldson, F. Matar, D. Hayes, M. Duman, D. Oldfield, M. Westerhausen and A. McDonagh, Gold Microstructures by Thermolysis of Gold(III) Di-isopropyldithiocarbamate Complexes, *ChemNanoMat*, 2024, **10**, e202300514.
258 M. Mäkelä, T. HatanpäÄ, K. Mizohata, J. Räisänen, M. Ritala and M. Leskelä, Thermal Atomic Layer Deposition of Continuous and Highly Conducting Gold Thin Films, *Chem. Mater.*, 2017, **29**, 6130–6136.
259 M. Contel, A. J. Edwards, J. Garrido, M. B. Hursthouse, M. Laguna and R. Terroba, Mesityl gold(III) complexes. X-ray structure of mononuclear $[Au(mes)_2Cl(PPh_3)]$ and the dimer $[Au(mes)_2Cl]_2$, *J. Organomet. Chem.*, 2000, **607**, 129–136.
260 J. Quero, S. Cabello, T. Fuertes, I. Mármol, R. Laplaza, V. Polo, M. C. Gimeno, J. Rodriguez-Yoldi and E. Cerrada, Proteasome versus Thioredoxin Reductase Competition as Possible Biological Targets in Antitumor Mixed Thiolate-Dithiocarbamate Gold(III) Complexes, *Inorg. Chem.*, 2018, **57**, 10832–10845.
261 A. Pettenuzzo, D. Montagner, P. McArdle and L. Ronconi, An innovative and efficient route to the synthesis of metal-based glycoconjugates: proof-of-concept and potential applications, *Dalton Trans.*, 2018, **47**, 10721–10736.

262 C. Nardon, D. Fregona, L. Brustolin and N. Pettenuzzo, Coordination compounds, syntheses, nanoformulation and use thereof in oncology, *World Intellectual Property Organization*, WO2018100561, 2017.

263 S. C. Bajia and A. Mishra, Synthesis and spectroscopic characterization of bis(N-alkyldithiocarbamato)nickel(II) complexes: crystal structures of $[Ni(S_2CNH(n\text{-}Pr))_2]$ and $[Ni(S_2CNH(i\text{-}Pr))_2]$, *J. Coord. Chem.*, 2011, **64**, 2727–2734.

264 A. Z. Halimehjani, K. Marjani, A. Ashouri and V. Amani, Synthesis and characterization of transition metal dithiocarbamate derivatives of 1-aminoadamantane: Crystal structure of (N-adamantyldithiocarbamato)nickel(II), *Inorg. Chim. Acta*, 2011, **373**, 282–285.

265 F. F. Bobinihi, D. C. Onwudiwe, A. C. Ekennia, O. C. Okpareke, C. Arderne and J. R. Lane, Group 10 metal complexes of dithiocarbamates derived from primary anilines: Synthesis, characterization, computational and antimicrobial studies, *Polyhedron*, 2019, **158**, 296–310.

266 C. E. Morrison, F. Wang, N. P. Rath, B. M. Wieliczka, R. A. Loomis and W. E. Buhro, Cadmium Bis(phenyldithiocarbamate) as a Nanocrystal Shell-Growth Precursor, *Inorg. Chem.*, 2017, **56**, 12920–12929.

267 L. H. van Poppel, T. L. Groy and M. T. Caudle, Carbon-Sulfur Bond Cleavage in Bis(N-alkyldithiocarbamato) cadmium(II) Complexes: Heterolytic Desulfurization Coupled to Topochemical Proton Transfer, *Inorg. Chem.*, 2004, **43**, 3180–3188.

268 A. A. Memon, M. Afzaal, M. A. Malik, C. Q. Nguyen, P. O'Brien and J. Raftery, The N-alkyldithiocarbamato complexes $[M(S_2CNHR)_2]$ (M = Cd(II) Zn(II); R = C_2H_5, C_4H_9, C_6H_{13}, $C_{12}H_{25}$); their synthesis, thermal decomposition and use to prepare of nanoparticles and nanorods of CdS, *Dalton Trans.*, 2006, 4499–4505.

269 D. C. Onwudiwe, T. Arfin, C. A. Strydom and R. J. Kriek, A study of the thermal and AC impedance properties of N-phenyldithiocarbamate complexes of Zn(II), *Electrochim. Acta*, 2013, **109**, 809–817.

270 B. B. Kaul and K. B. Pandeya, N-Monoaryldithiocarbamatecobalt(III) complexes, *Transition Met. Chem.*, 1979, **4**, 112–114.

271 G. L. Zhang, Y. T. Li and Z. Y. Wu, Tris(ethyldithiocarbamato-κ^2S,S′)cobalt(III), *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m350–m351.

272 E. Tejeria, J. Giglio, L. Fernandez and A. Rey, Development and evaluation of a ^{99m}Tc(V)-nitrido complex derived from estradiol for breast cancer imaging, *Appl. Radiat. Isot.*, 2019, **154**, 108854.

273 X. Song, Y. Wang, J. Zhang, Z. Jin, W. Zhang and Y. Zhang, Synthesis and evaluation of a novel ^{99m}Tc nitrido radiopharmaceutical with alendronate dithiocarbamate as a potential bone-imaging agent, *Chem. Biol. Drug Des.*, 2018, **91**, 545–551.

274 Y. Chen, H. Guo, F. Xie and J. Lu, Preparation and biological evaluation of ^{99m}TcN-labeled pteroyl-lys derivative as a potential folate receptor imaging agent, *J. Labelled Compd. Radiopharm.*, 2014, **57**, 12–17.

275 N. Hollingsworth, A. Roffey, H. U. Islam, M. Mercy, A. Roldan, W. Bras, M. Wolthers, C. R. A. Catlow, G. Sankar, G. Hogarth and N. H. De Leeuw, Active Nature of Primary Amines during Thermal Decomposition of Nickel Dithiocarbamates to Nickel Sulfide Nanoparticles, *Chem. Mater.*, 2014, **26**, 6281–6292.

276 R. Wong and S. J. Dolman, Isothiocyanates from Tosyl Chloride Mediated Decomposition of in Situ Generated Dithiocarbamic Acid Salts, *J. Org. Chem.*, 2007, **72**, 3969–3971.

277 N. Sun, B. Li, J. Shao, W. Mo, B. Hu, Z. Shen and X. Hu, A general and facile one-pot process of isothiocyanates from amines under aqueous conditions, *Beilstein J. Org. Chem.*, 2012, **8**, 61–70.

278 Z. Fu, W. Yuan, N. Chen, Z. Yang and J. Xu, $Na_2S_2O_8$-mediated efficient synthesis of isothiocyanates from primary amines in water, *Green Chem.*, 2018, **20**, 4484–4491.

279 M. A. Agoro and E. L. Meyer, FeS/FeS_2 nanoscale structures synthesized in one step from Fe(ll) dithiocarbamate complexes as a single source precursor, *Front. Chem.*, 2022, **10**, 1035594.

280 A. M. Paca and P. A. Ajibade, Synthesis and structural studies of iron sulphide nanocomposites prepared from Fe(III) dithiocarbamates single source precursors, *Mater. Chem. Phys.*, 2017, **202**, 143–150.

281 M. Tarique and M. Aslam, Synthesis and characterization of some transition metal complexes of dithiocarbamate ligand derived from p-toluidine, *Asian J. Chem.*, 2010, **22**, 2031–2034.

282 M. A. Agoro and E. L. Meyer, Influence of a One-Pot Approach on a Prepared CuS Macro/Nanostructure from Various Molecular Precursors, *Inorganics*, 2023, **11**, 266.

283 E. I. Duran-Garcia, J. Martinez-Santana, N. Torres-Gomez, A. R. Vilchis-Nestor and I. Garcia-Orozco, Copper sulfide nanoparticles produced by the reaction of N-alkyldithiocarbamatecopper(II) complexes with sodium borohydride, *Mater. Chem. Phys.*, 2021, **269**, 124743.

284 N. L. Botha and P. A. Ajibade, Effect of temperature on crystallite sizes of copper sulfide nanocrystals prepared from copper(II) dithiocarbamate single source precursor, *Mater. Sci. Semicond. Process.*, 2016, **43**, 149–154.

285 C. Chen, K.-W. Yang, L. Zhai, H.-H. Ding and J.-Z. Chigan, Dithiocarbamates combined with copper for revitalizing meropenem efficacy against NDM-1-producing Carbapenem-resistant Enterobacteriaceae, *Bioorg. Chem.*, 2022, **118**, 105474.

286 S. Huang, X. Xu, J. C. Sarker, D. Pugh and G. Hogarth, Primary-amine-derived Cu(I)-dithiocarbamate complexes and their use as low temperature single source precursors to CuS (covellite) nanomaterials, *Dalton Trans.*, 2024, **53**, 17140–17145.

287 C. Bianchini, C. A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, Reactivity of copper(I) tetrahydroborates toward carbon disulfide and phenyl isothiocyanate. Structures of $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$,

$(PPh_3)_2Cu(S_2COEt)$, and $(PPh_3)_2Cu(S_2CNHPh)$, *Inorg. Chem.*, 1985, **24**, 932–939.

288 Q. Gaydon and S. D. Bohle, Coordination Chemistry of the Parent Dithiocarbamate $H_2NCS_2^-$: Organometallic Chemistry and Tris-Chelates of Group 9 Metals, *Inorg. Chem.*, 2022, **61**, 4660–4672.

289 C. L. Teske and W. Bensch, On Crystal Structure Investigations of α- and β-Ammoniumdithiocarbamate $NH_4CS_2NH_2$ and the Role of Hydrogen Bonding, *Z. Anorg. Allg. Chem.*, 2010, **636**, 356–362.

290 L. Capacchi, M. Nardelli and A. Villa, The crystal structure of nickel(II) bis(dithiocarbamate), *Chem. Commun.*, 1966, **441**.

291 M. A. Bernard, M. M. Borel and J. Gallay, Metal dithiocarbamates. III. Crystallographic study of zinc dithiocarbamate, *Bull. Soc. Chim. Fr.*, 1969, **9**, 3069.

292 C. L. Teske and W. Bensch, On Tris(dithiocarbamato)-Chromium(III), $Cr(S_2CNH_2)_3$, *Z. Anorg. Allg. Chem.*, 2012, **638**, 2093–2097.

293 C. L. Raston, A. H. White and A. C. Willis, Crystal structure of tris(dithiocarbamato)cobalt(III), *J. Chem. Soc., Dalton Trans.*, 1975, 2429–2432.

294 C. L. Teske and W. Bensch, On Mono(dithiocarbamato)-silver(I), AgS_2CNH_2, *Z. Anorg. Allg. Chem.*, 2015, **641**, 1031–1035.

295 C. L. Teske, H. Reinsch, H. Terraschke and W. Bensch, Synthesis, Crystal Structure and Selected Properties of Mono(dithiocarbamato)-gold(I), AuS_2CNH_2, *Z. Anorg. Allg. Chem.*, 2017, **643**, 466–470.

296 C. L. Teske, A.-L. Hansen, R. Weihrich, L. Kienle, M. Kamp, K. P. van der Zwan, J. Senker, C. Dosche, G. Wittstock and W. Bensch, Synthesis, Crystal Structure, and Selected Properties of $[Au(S_2CNH_2)_2]SCN$: A Precursor for Gold Macro-Needles Consisting of Gold Nanoparticles Glued by Graphitic Carbon Nitride, *Chem. – Eur. J.*, 2019, **25**, 6763–6772.

297 C. L. Teske, On Ammonium-bis(dithiocarbamato)-copper(I)-monohydrate and Mono(dithiocarbamato)-copper(I), *Z. Anorg. Allg. Chem.*, 2013, **639**, 2767–2773.

298 M. A. Agoro and E. L. Meyer, Roles of TOPO Coordinating Solvent on Prepared Nano-Flower/Star and Nano-Rods Nickel Sulfides for Solar Cells Applications, *Nanomaterials*, 2022, **12**, 3409.

299 M. A. Agoro and E. L. Meyer, Influence of a One-Pot Approach on a Prepared CuS Macro/Nanostructure from Various Molecular Precursors, *Inorganics*, 2023, **11**, 266.

300 M. A. Agoro, E. L. Meyer and O. I. Olayiwola, Assemble of porous heterostructure thin film through CuS passivation for efficient electron transport in dye-sensitized solar cells, *Discover Nano*, 2024, **19**, 130.

301 M. A. Agoro, E. L. Meyer, J. Z. Mbese and K. Manu, Electrochemical fingerprint of CuS-hexagonal chemistry from (Bis(N-1,4-Phenyl-N-(4-morpholinedithiocarbamato) copper(II) complexes) as photon absorber in quantum-dot/Dye-sensitised solar cells, *Catalysts*, 2020, **10**, 300.

302 M. M. Salman, A. A. Al-Dulaimi, A. S. M. Al-Janabi and M. A. Alheety, Novel dithiocabamate nano Zn(II), Cd(II) and Hg(II) complexes with pyrrolidinedithiocarbamate and N,N-diethyldithiocarbamate, *Mater. Today: Proc.*, 2021, **43**, 863–868.

303 P. A. Ajibade, D. C. Onwudiwe and M. J. Moloto, Synthesis of hexadecylamine capped nanoparticles using group 12 complexes of N-alkyl-N-phenyl dithiocarbamate as single-source precursors, *Polyhedron*, 2011, **30**, 246–252.

304 D. C. Onwudiwe and P. A. Ajibade, Synthesis and Crystal Structure of Bis(N-alkyl-N-phenyl dithiocarbamato) mercury(II), *J. Chem. Crystallogr.*, 2011, **41**, 980–985.

305 D. C. Onwudiwe, Y. B. Nthwane, A. C. Ekennia and E. Hosten, Synthesis, characterization and antimicrobial properties of some mixed ligand complexes of Zn(II) dithiocarbamate with different N-donor ligands, *Inorg. Chim. Acta*, 2016, **447**, 134–141.

306 P. A. Ajibade and D. C. Onwudiwe, Synthesis and characterization of group 12 complexes of N,N-methyl phenyl-N, N-butyl phenyl dithiocarbamate, *J. Coord. Chem.*, 2011, **64**, 2963–2973.

307 E. L. Meyer and M. A. Agoro, Impact of FeS on the TiO_2 Layer As Support System in QDSCs, *ACS Omega*, 2024, **9**, 37891–37900.

308 M. A. Agoro and E. L. Meyer, FeS/FeS_2 nanoscale structures synthesized in one step from Fe(ll) dithiocarbamate complexes as a single source precursor, *Front. Chem.*, 2022, **10**, 1035594.

309 M. A. Agoro and E. L. Meyer, Coating of CoS on hybrid anode electrode with enhance performance in hybrid dye-sensitized solar cells, *Electrochim. Acta*, 2024, **502**, 144877.

310 M. A. Agoro, J. Z. Mbese and E. L. Meyer, Inorganic Pb(II)-P and Pb(II)-S Complexes as Photosensitizers from Primary and Secondary Amines in Dyes-Sensitized Solar Cells, *ACS Omega*, 2021, **6**, 23700–23709.

311 M. A. Agoro, J. Z. Mbese and E. L. Meyer, Electrochemistry of Inorganic OCT-PbS/HDA and OCT-PbS Photosensitizers Thermalized from Bis(N-diisopropyl-N-octyldithiocarbamato) Pb(II) Molecular Precursors, *Molecules*, 2020, **25**, 1919.

312 J. Z. Mbese, E. L. Meyer and M. A. Agoro, Electrochemical performance of photovoltaic cells using HDA capped-SnS nanocrystal from bis (N-1,4-phenyl-N-morpho-dithiocarbamato) Sn(II) complexes, *Nanomaterials*, 2020, **10**, 414.

313 E. L. Meyer, J. Z. Mbese, M. A. Agoro and R. Taziwa, Optical and structural-chemistry of SnS nanocrystals prepared by thermal decomposition of bis(N-di-isopropyl-N-octyl dithiocarbamato)tin(II) complex for promising materials in solar cell applications, *Opt. Quantum Electron.*, 2020, **52**, 90.

314 J. Z. Mbese, E. L. Meyer and M. A. Agoro, Electrocatalytic properties of PbS nanocrystals structured from (bis(N-1,4-phenyl-N-(4-morpholine)dithiocarbamato Pb(II) complexes) as photosensitizer for quantum-dots-sensitized solar cells, *Mater. Lett.*, 2020, **271**, 127770.

315 M. A. Agoro, E. L. Meyer, J. Z. Mbese, X. Fuku and C. C. Ahia, Aliphatic mixed ligands Sn(II) complexes as photon absorbers in quantum dots sensitized solar cell, *J. Solid State Chem.*, 2022, **308**, 122890.

316 L. K. Macreadie, C. M. Forsyth, D. R. Turner and A. S. R. Chesman, Cadmium tris(dithiocarbamate) ionic liquids as single source, solvent-free cadmium sulfide precursors, *Chem. Commun.*, 2018, **54**, 8925–8928.

317 H. L. M. Van Gaal, J. W. Diesveld, F. W. Pijpers and J. G. M. Van der Linden, Carbon-13 NMR spectra of dithiocarbamates. Chemical shifts, carbon-nitrogen stretching vibration frequencies and π-bonding in the NCS_2 fragment, *Inorg. Chem.*, 1979, **18**, 3251–3260.

318 M. Moriyasu and Y. Hashimoto, Kinetic studies of fast equilibrium by high-performance liquid chromatography. I. Ternary complex formation of N,N-disubstituted dithiocarbamate chelates of nickel(II) and copper(II), *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3590–3595.

319 M. Moriyasu and Y. Hashimoto, Kinetic studies on the labile ternary nickel(II) chelates of N-disubstituted dithiocarbamic acids by high-performance liquid chromatography, *Chem. Lett.*, 1980, 117–120.

320 M. Moriyasu and Y. Hashimoto, Kinetic studies of fast equilibrium by means of high-performance liquid chromatography. II. Ligand exchange of N,N-disubstituted dithiocarbamate chelates of Ni(II), *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2470–2474.

321 O. Liska, G. Guiochon and H. Colin, Liquid chromatography of metal complexes of N-disubstituted dithiocarbamic acids. I. High-performance liquid chromatography of nickel(II) bisdialkyldithiocarbamates, *J. Chromatogr.*, 1979, **171**, 145–151.

322 O. Liska, J. Lehotay, E. Brandsteterova and G. Guiochon, Liquid chromatography of metal complexes of N-disubstituted dithiocarbamic acids. II. Identification of nickel(II) bisdialkyldithiocarbamate mixed-ligand complexes, *J. Chromatogr.*, 1979, **171**, 153–159.

323 S. Dilli and P. Tong, Liquid chromatography of metal chelates. Chromatographic studies of homologous dialkyldithiocarbamates, *Anal. Chim. Acta*, 1999, **395**, 101–112.

324 E. Beinrohr and J. Garaj, NMR study of ligand exchange in some metal dithiocarbamates, *Collect. Czech. Chem. Commun.*, 1980, **45**, 1785–1792.

325 M. Moriyasu and Y. Hashimoto, Kinetic studies of fast equilibrium by means of high-performance liquid chromatography. III. Ternary complex formation between nickel (II) diethyldithiocarbamate and other unlike nickel(II) chelates, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3374–3378.

326 N. V. Duffy, Ligand exchange in tris(diorganodithiocarbamato)iron(III) complexes, *Inorg. Chim. Acta*, 1981, **47**, 31–35.

327 K. Drabent and L. Latos-Grazynski, NMR studies of mixed-ligand iron(III) dithiocarbamates, *Polyhedron*, 1985, **4**, 1637–1641.

328 R. Chant, A. R. Hendrickson, R. L. Martin and N. M. Rohde, Tris(dithiocarbamato) complexes of iron(II), iron(III), and iron(IV). Electrochemical study, *Inorg. Chem.*, 1975, **14**, 1894–1902.

329 A. M. Bond, R. Colton, D. Dakternieks, M. L. Dillon, J. Hauenstein and J. E. Moir, Phosphorus-31, cadmium-113 and mercury-199 NMR studies on dithiolate complexes of cadmium and mercury and their phosphine adducts, *Aust. J. Chem.*, 1981, **34**, 1393–1400.

330 A. M. Bond, R. Colton, M. L. Dillon, J. E. Moir and D. R. Page, Investigation of exchange and redox reactions of mercury dithiocarbamate complexes by electrochemical techniques at mercury electrodes, mercury-199 nuclear magnetic resonance spectrometry and mass spectrometry, *Inorg. Chem.*, 1984, **23**, 2883–2891.

331 M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que Jr and L. H. Pignolet, Dynamic stereochemistry of tris(chelate) complexes. I. Tris(dithiocarbamato) complexes of iron, cobalt, and rhodium, *J. Am. Chem. Soc.*, 1973, **95**, 4537–4545.

332 A. R. Hendrickson, R. L. Martin and D. Taylor, Synthesis and properties of dimeric cobalt(III) dithiocarbamate complexes $[Co_2(R_2dtc)_5]^+$. X-ray structural analysis of pentakis (diethyldithiocarbamato)dicobalt(III) tetrafluoroborate, *J. Chem. Soc., Dalton Trans.*, 1975, 2182–2188.

333 A. M. Bond, R. Colton, J. E. Moir and D. R. Page, Investigations of mixed-ligand cobalt dithiocarbamate complexes by cobalt-59 nuclear magnetic resonance spectroscopy, mass spectrometry, and electrochemistry, *Inorg. Chem.*, 1985, **24**, 1298–1302.

334 F. Artizzu, L. Marchio, L. Pilia, A. Serpe and P. Deplano, Heteroleptic Co(III) bisdithiocarbamato-dithione complexes: Synthesis, structure and bonding of $[Co(Et_2dtc)_2(R_2pipdt)]BF_4$ (R = Me, 1; Ph, 2; pipdt = piperazin-2,3-dithione) complexes, *J. Coord. Chem.*, 2022, **75**, 2434–2447.

335 A. A. Olanrewaju, F. S. Fabiyi, C. U. Ibeji, E. G. Kolawole and R. Gupta, Synthesis, spectral, structure and computational studies of novel transition Metal(II) complexes of (Z)-((dimethylcarbamothioyl)thio) ((1,1,1-trifluoro-4-(naphthalen-2-yl)-4-oxobut-2-en-2-yl)oxy), *J. Mol. Struct.*, 2020, **1211**, 128057.

336 A. A. Olanrewaju, C. U. Ibeji and O. E. Oyeneyin, Biological evaluation and molecular docking of some newly synthesized 3d-series metal(II) mixed-ligand complexes of fluoro-naphthyl diketone and dithiocarbamate, *SN Appl. Sci.*, 2020, **2**, 678.

337 A. C. Ekennia, D. C. Onwudiwe, L. O. Olasunkanmi, A. A. Osowole and E. E. Ebenso, Synthesis, DFT calculation, and antimicrobial studies of novel Zn(II), Co(II), Cu (II), and Mn(II) heteroleptic complexes containing benzoylacetone and dithiocarbamate, *Bioinorg. Chem. Appl.*, 2015, 1–13.

338 A. C. Ekennia, D. C. Onwudiwe, A. A. Osowole, L. O. Olasunkanmi and E. E. Ebenso, *J. Chem.*, 2016, 5129010.

339 E. V. Ignatov, L. E. Zelenkov, S. V. Baykov, M. K. Shurikov, A. V. Semenov, N. A. Bokach, P. S. Postnikov and V. Yu. Kukushkin, Controlled Mono- and Double-Insertion of Sulfonamide Fragments into Ni–S Bonds of

Nickel(II) Dithiocarbamate Complexes via Sulfonyl Azide Reactivity, *Inorg. Chem.*, 2025, **64**, 11867–11879.

340 G. Exarchos and S. D. Robinson, Constitution of some “dithiocarbamato-bridged heterobimetallic complexes”, *Polyhedron*, 1997, **16**, 1573–1576.

341 G. Exarchos, S. C. Nyburg and S. D. Robinson, The synthesis and characterization of $[Pd(S_2CNEt_2)(Ph_2PCH_2CH_2PPh_2)]^+$ salts of some chloro- and bromo-metalate anions- X-ray crystal structures of $[Pd(S_2CNEt_2)(Ph_2PCH_2CH_2PPh_2)]^+[MCl_2]^-$(M = Cu, Ag), *Polyhedron*, 1998, **17**, 1257–1266.

342 G. Exarchos, S. D. Robinson and J. W. Steed, The synthesis and characterisation of $[Pd(S_2CNEt_2)\{Ph_2P(CH_2)_nPPh_2\}]^+$ salts of some chlorometallate anions (n = 1, 3, 4): X-ray crystal structures of the salts $[Pd(S_2CNEt_2)\{Ph_2P(CH_2)_nPPh_2\}]_2[MCl_4]$ (n = 1, 4; M = Cd; n = 3; M = Hg), *Polyhedron*, 2000, **19**, 1511–1517.

343 G. Exarchos, S. D. Robinson and J. W. Steed, The synthesis of new bimetallic complex salts by halide/sulfur chelate cross transfer: X-ray crystal structures of the salts $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$, $[Co(S_2CNEt_2)_2(dppe)]_2$ $[Cl_3ZnO:(Ph)_2PCH_2CH_2P(Ph)_2:OZnCl_3]$ and $[Pd(S_2CN^nBu_2)(bipy)]_2[CdCl_4]$, *Polyhedron*, 2001, **20**, 2951–2963.

344 T. Torimoto, T. Adachi, K.-I. Okazaki, M. Sakuraoka, T. Shibayama, B. Ohtani, A. Kudo and S. Kuwabata, Facile Synthesis of ZnS-$AgInS_2$ Solid Solution Nanoparticles for a Color-Adjustable Luminophore, *J. Am. Chem. Soc.*, 2007, **129**, 12388–12389.

345 T. Kameyama, T. Takahashi, T. Machida, Y. Kamiya, T. Yamamoto, S. Kuwabata and T. Torimoto, Controlling the Electronic Energy Structure of ZnS-$AgInS_2$ Solid Solution Nanocrystals for Photoluminescence and Photocatalytic Hydrogen Evolution, *J. Phys. Chem. C*, 2015, **119**, 24740–24749.

346 W. Hoisang, T. Uematsu, T. Torimoto and S. Kuwabata, Luminescent Quaternary $Ag(In_xGa_{1(-x)})S_2/GaS_y$ Core/Shell Quantum Dots Prepared Using Dithiocarbamate Compounds and Photoluminescence Recovery via Post Treatment, *Inorg. Chem.*, 2021, **60**, 13101–13109.

347 T. Uematsu, M. Tepakidareekul, T. Hirano, T. Torimoto and S. Kuwabata, Facile High-Yield Synthesis of Ag-In-Ga-S Quaternary Quantum Dots and Coating with Gallium Sulfide Shells for Narrow Band-Edge Emission, *Chem. Mater.*, 2023, **35**, 1094–1106.

348 E. J. Mensforth, M. R. Hill and S. R. Batten, Coordination polymers of sulphur-donor ligands, *Inorg. Chim. Acta*, 2013, **403**, 9–24.

349 M. Ebihara, K. Tokoro, M. Maeda, M. Ogami, K. Imaeda, K. Sakurai, H. Masuda and T. Kawamura, Bonding interaction between group 10 and 11 metals. Synthesis, structure and properties of $[M_3(S_2CNR_2)_6M'_2]^{2+}$ (M = Pt or Pd; M′ = Ag or Cu; R = Et, Pr^i, Pr^n, Bu^n or C_6H_{11}), *J. Chem. Soc., Dalton Trans.*, 1994, 3621–3635.

350 J. Fornies, A. Martin, R. Navarro, V. Sicilia, P. Villarroya and A. G. Orpen, Nucleophilic behavior of the neutral complexes $[M(C\,\hat{}\,P)(S_2CNMe_2)]$ [M = Pd, Pt; $C\,\hat{}\,P = CH_2C_6H_4P(C_6H_4Me\text{-}o)_2\text{-}\kappa\text{-}C,P$] towards Ag(I) and Au(I) compounds. Synthesis (M = Pd, Pt) and molecular structures (M = Pt) of polynuclear complexes containing M-Ag and M-S bonds, *J. Chem. Soc., Dalton Trans.*, 1998, 3721–3726.

351 K. Himoto, T. Horii, S. Oda, S. Suzuki, K. Sugimoto, T. Okubo, M. Maekawa and T. Kuroda-Sowa, Crystal structure of a new mixed-metal coordination polymer consisting of NiII piperidine-dithiocarbamate and pentanuclear CuI-I cluster units, *Acta Crystallogr., Sect. E:Crystallogr. Commun.*, 2018, **74**, 233–236.

352 T. Ikada, S. Kuwata, Y. Mizobe and M. Hidai, Syntheses and Structures of Mixed-Metal Sulfido Clusters Containing Incomplete Cubane-Type $M_2M'S_4$ and Cubane-Type $M_2M'_2S_4$ Cores (M = Mo, W; M′ = Rh, Ir), *Inorg. Chem.*, 1999, **38**, 64–69.

353 H. Brunner, A. Hollman, M. Zabel and B. Nuber, The ligand $[Cp_2MoH_2]$ in complexes with Ag-S bonds, *J. Organomet. Chem.*, 2000, **609**, 44–52.

354 K. Ramasamy, M. A. Malik, N. Revaprasadu and P. O'Brien, Routes to Nanostructured Inorganic Materials with Potential for Solar Energy Applications, *Chem. Mater.*, 2013, **25**, 3551–3569.

355 K. Ramasamy, M. A. Malik and P. O'Brien, Routes to Copper Zinc Tin Sulfide Cu_2ZnSnS_4 a Potential Material for Solar Cells, *Chem. Commun.*, 2012, **48**, 5703–5714.

356 J. A. O. Hill and R. J. Magee, R. J. The Thermochemistry of the Metal Dithiocarbamate and Xanthate Complexes, *Rev. Inorg. Chem.*, 1981, **4**, 141–197.

357 J. O. Hill, J. P. Murray and K. C. Patel, The Thermochemistry of the Metal Dithiocarbamate and Xanthate Complexes - A Review Up-date, *Rev. Inorg. Chem.*, 1994, **14**, 363–387.

358 A. K. Sharma, Thermal Behaviour of Metal-Dithiocarbamates, *Thermochim. Acta*, 1986, **104**, 339–372.

359 S. K. Sengupta and S. Kumar, Thermal studies on metal dithiocarbamato complexes. A review, *Thermochim. Acta*, 1984, **72**, 349–361.

360 S. T. Breviglieri, E. T. G. Cavalheiro and G. O. Chierice, Correlation Between Ionic Radius and Thermal Decomposition of Fe(II), Co(II), Ni(II), Cu(II) And Zn(II) Diethanoldithiocarbamates, *Thermochim. Acta*, 2000, **356**, 79–84.

361 L. Xi, D. Y. Cho, M. Duchamp, C. B. Boothroyd, J. Y. Lek, A. Besmehn, R. Waser, Y. M. Lam and B. Kardynal, Understanding the Role of Single Molecular ZnS Precursors in the Synthesis of In(Zn)P/ZnS Nanocrystals, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18233–18242.

362 P. B. Mann, I. J. McGregor, S. Bourke, M. Burkitt-Gray, S. Fairclough, M. T. Ma, G. Hogarth, M. Thanou, N. Long and M. Green, An Atom Efficient, Single source Precursor Route to Plasmonic CuS Nanocrystals, *Nanoscale Adv.*, 2019, **1**, 522–526.

363 K. Ramasamy, M. A. Malik and P. O'Brien, The Chemical Vapor Deposition of Cu_2ZnSnS_4 Thin Films, *Chem. Sci.*, 2011, **2**, 1170–1172.

364 P. Kevin, M. A. Malik, P. O'Brien, J. Cameron, R. G. Taylor, N. J. Findlay, A. R. Inigo and P. J. Skabara, Nanoparticles of Cu_2ZnSnS_4 as Performance Enhancing Additives for Organic Field-Effect Transistors, *J. Mater. Chem. C*, 2016, **4**, 5109–5115.

365 T. Uematsu, M. Tepakidareekul, T. Hirano, T. Torimoto and S. Kuwabata, Facile High-Yield Synthesis of Ag-In-Ga-S Quaternary Quantum Dots and Coating with Gallium Sulfide Shells for Narrow Band-Edge Emission, *Chem. Mater.*, 2023, **35**, 1094–1106.

366 W. Hoisang, T. Uematsu, T. Torimoto and S. Kuwabata, Luminescent Quaternary $Ag(In_xGa_{1(-x)})S_2/GaS_y$ Core/Shell Quantum Dots Prepared Using Dithiocarbamate Compounds and Photoluminescence Recovery via Post Treatment, *Inorg. Chem.*, 2021, **60**, 13101–13109.

367 K. S. Ahmad, S. B. Jaffri, H. Panchal, R. K. Gupta, M. A. Abdel-Maksoud, A. Malik and W. H. Al-Qahtani, Advancing energy storage and producing potential with a single source driven semiconducting BaS_3:Cs_2S:La_2S_3 chalcogenide prepared via a sustainable mode, *New J. Chem.*, 2025, **49**, 2291–2307.

368 K. S. Ahmad, S. B. Jaffri, K. Chaudhary, R. K. Gupta, G. A. Ashraf and N. H. Alotaibi, Harnessing energy sustainability: synthesis of BaS_2:CoS:MnS semiconductor trichotomous chalcogenide for superior supercapacitor device operation, *Ionics*, 2025, **31**, 2109–2122.

369 K. S. Ahmad, S. B. Jaffri, B. Makawana, R. K. Gupta, G. A. Ashraf and M. Altaf, Sustainable Semiconducting BaS_3:Sb_2S_3:LaS_2 Filiform Rods: Revolutionizing Energy Storage and Production With Mixed Metal Chalcogenides, *Appl. Organomet. Chem.*, 2025, **39**, e7880.

370 S. B. Jaffri, K. S. Ahmad, J. S. Al-Hawadi, B. Makawana, R. K. Gupta, G. A. Ashraf and M. K. Okla, Revolutionizing energy storage and electro-catalysis: unleashing electrode power with novel BaS_3:La_2S_3:Ho_2S_3 synthesized from single-source precursors for enhanced electrochemical functionality, *J. Sol-Gel Sci. Technol.*, 2025, **113**, 197–212.

371 S. B. Jaffri, K. S. Ahmad, B. Makawana, R. K. Gupta, M. A. Abdel-Maksoud, A. Malik and W. H. Al-Qahtani, Amplifying energy storage and production efficiency: Utilizing BaS_3: Ni_2S_3: Sb_2S_3 synthesized from dithiocarbamate precursors for enhanced and sustainable energy solutions, *J. Phys. Chem. Solids*, 2025, **196**, 112394.

372 R. Yang, J. Nelson, C. Fai, H. A. Yetkin, C. Werner, M. Tervil, A. D. Jess, P. J. Dale and C. J. Hages, A Low-Temperature Growth Mechanism for Chalcogenide Perovskites, *Chem. Mater.*, 2023, **35**, 4743–4750.

373 A. E. Dixon, New benzylic derivatives of thiocarbamide, *J. Chem. Soc., Dalton Trans.*, 1891, **59**, 551–569.

