



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

Received 8th May 2025,
Accepted 19th June 2025

DOI: 10.1039/d5dt01085c

rsc.li/dalton

Addressing misconceptions in dithiocarbamate chemistry

David Pugh  and Graeme Hogarth  *

Dithiocarbamates are monoanionic chelating ligands, easily prepared from CS₂ 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 cuproptosis,⁵³ the anti-cancer activity of [Cu(S₂CNEt₂)₂], which has been known for over 40 years,^{54–59} has once again come under the spotlight.^{60–64} Thus, tetraethyl thiuram disulfide (Et₄TDS), 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 blood⁶⁶ to give diethyldithiocarbamate, which in turn can bind to Cu(II) to afford [Cu(S₂CNEt₂)₂] *in situ*.

Dithiocarbamates are easily prepared, generally in high yields, upon reaction of CS₂ 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 “dithio-

carbamate” in SciFinder® giving almost 25 000 hits and for “dithiocarbamate” 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 CS₂ to afford the dithiocarbamate

Primary and secondary amines are extremely basic, having p*K*_bs of *ca.* 4. Consequently, they are not acidic and have p*K*_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 CS₂.⁷³ 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



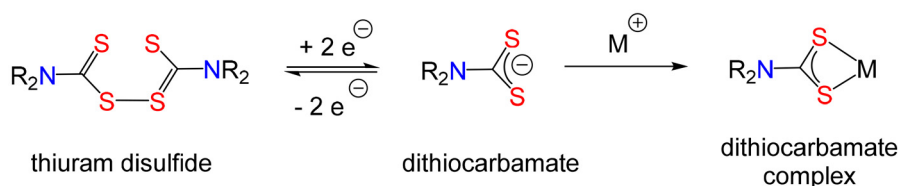


Fig. 1 Dithiocarbamates, their complexes and thiuram disulfides.

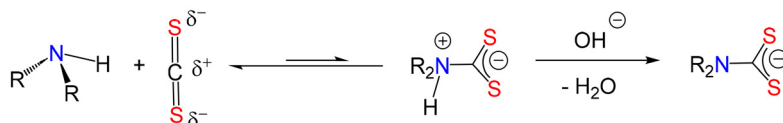


Fig. 2 Reaction of secondary amine with CS₂ in the presence of MOH as a base.

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 $[\text{NR}_2]^-$ or $[\text{NHR}]^-$ 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, CS₂ reacts with a primary or secondary amine to afford the dithiocarbamic acid

Many secondary and primary amines react directly with CS₂ 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 CS₂.^{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 (HexNH₂) and the dithiocarbamic acid, HexNHCS₂H⁷⁸ 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 $^1\text{Bu}_2\text{NH}$ 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 $\text{NaS}_2\text{CNBu}_2$.

Nice illustrations of an amine acting as both a base and a nucleophile are in the reaction of diamines with CS₂. For example, reaction of piperazine with CS₂ 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 CS₂ in the presence of MOH afford diaryldithiocarbamates

Anilines are nucleophilic enough to react directly with CS₂ and thus dithiocarbamates, [ArNHCS₂][−] are readily available.⁸⁷ In contrast, diphenylamine and other diarylamines are not nucleophilic enough and will not react directly with CS₂ in the presence of standard bases. Thus, to prepare [Ar₂NCS₂][−], the corresponding amides [NAr₂][−] need to be accessed; these are nucleophilic enough to react with CS₂. Reagents that are basic

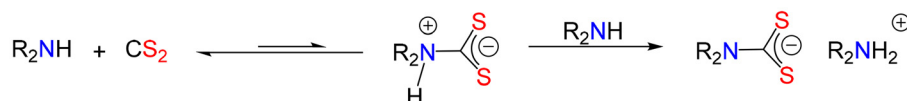


Fig. 3 Reaction of secondary amine with CS₂ in the absence of a second base.

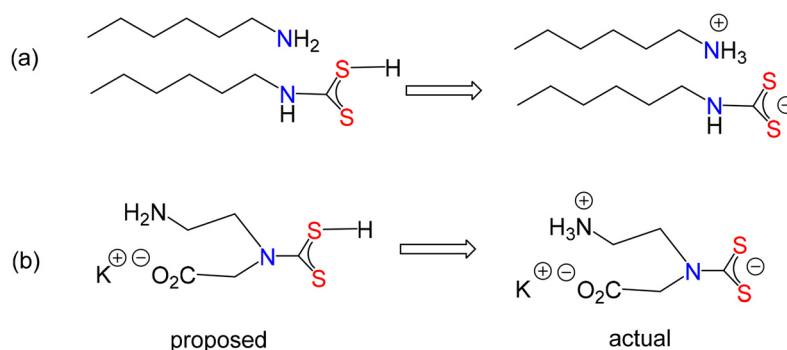


Fig. 4 Actual and proposed forms of crystallographically characterised "dithiocarbamic acids".

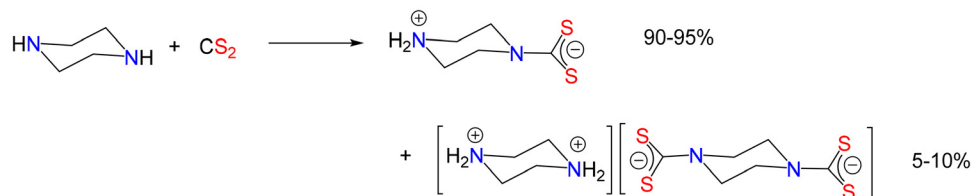


Fig. 5 Reaction of piperazine with CS_2 .

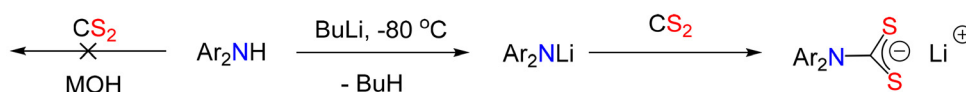


Fig. 6 Generation of diaryldithiocarbamate salts upon addition of CS_2 to LiNAr_2 .

enough to deprotonate Ar_2NH include $^n\text{BuLi}$,^{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 preparation⁸⁸ that uses $^n\text{BuLi}$ in thf to afford LiNAr_2 at low temperatures, which in turn react with CS_2 to form $\text{LiS}_2\text{CNAr}_2$ (essentially) quantitative yields⁶⁷ (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 $\text{KS}_2\text{CNH}(\text{CHO})$.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*

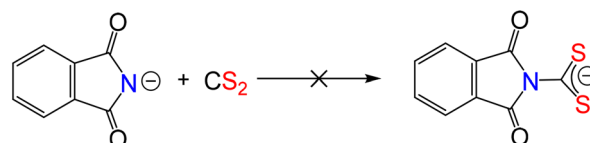


Fig. 7 Unsuccessful reaction of phthalimide with CS_2 .



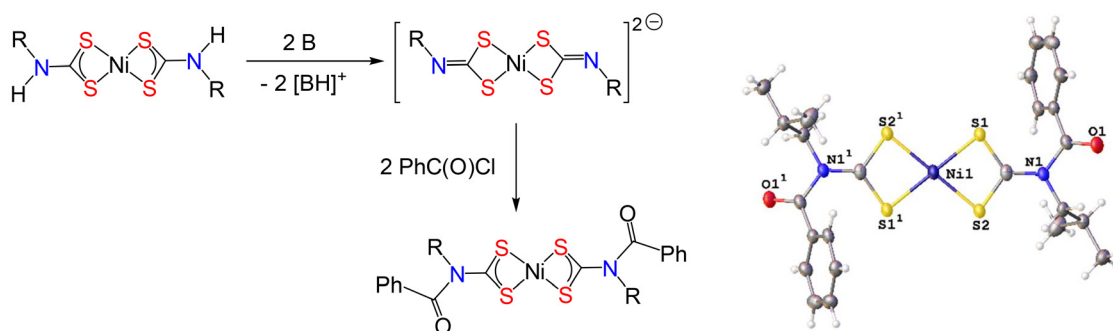


Fig. 8 Synthesis and molecular structure ($R = {}^i\text{Bu}$) of amide-functionalised nickel bis(dithiocarbamate) complex.

dithiocarbamate complexes.¹⁰³ For example, deprotonation of the corresponding primary amine-derived nickel complexes, $[\text{Ni}(\text{S}_2\text{CNHR})_2]$, 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 unstable¹¹⁹ 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 $[\text{M}(\text{S}_2\text{CNR}_2)_2]$ ($\text{M} = \text{Zn}, \text{Cd}$) 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.

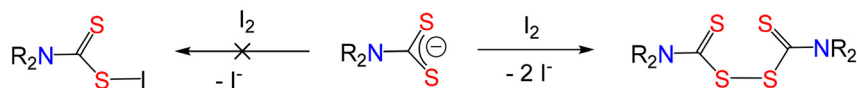


Fig. 10 I_2 oxidation of dithiocarbamate to thiuram disulfide.

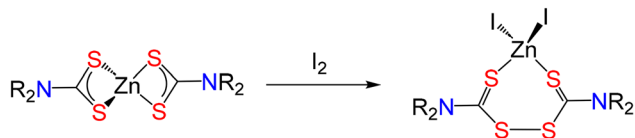


Fig. 11 I_2 addition to $[Zn(S_2CNR_2)_2]$ and formation of a thiuram disulfide complex.

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 $[Ti(S_2CNPr_2)_4]$ 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 $[Ti(CO)_4(S_2CNR_2)_2]^-$ 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 characterised¹⁵² 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 $[V(S_2CNR_2)_2]$, namely vanadyl complexes $[VO(S_2CNR_2)_2]$, are easily prepared¹⁵⁶ and have been extensively investigated as potential insulin mimetics¹⁵⁷ and molecular qubits.¹⁵⁸ Thus, akin to the titanium chemistry, even the

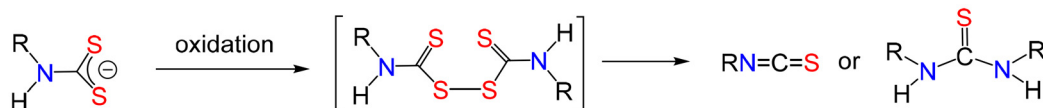


Fig. 12 Formation and decomposition of primary amine thiuram disulfides.



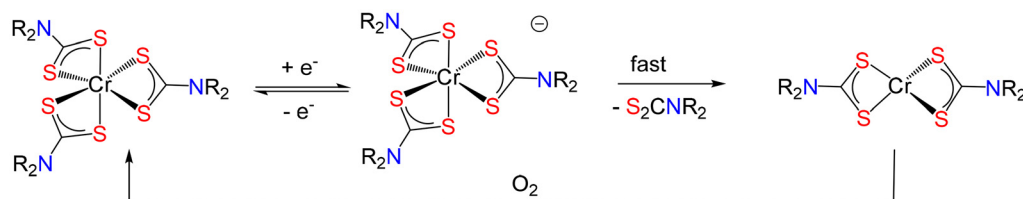


Fig. 13 Formation of $[\text{Cr}(\text{S}_2\text{CNR}_2)_2]_2$ via reduction of $[\text{Cr}(\text{S}_2\text{CNR}_2)_3]$ and back oxidation.

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, $[\text{Cr}(\text{S}_2\text{CNR}_2)_3]$ that are isolated.^{159–161} The first synthesis of $[\text{Cr}(\text{S}_2\text{CNET}_2)_2]$ 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 $[\text{Cr}(\text{CO})_6]$ and $[\text{Hg}(\text{S}_2\text{CNET}_2)_2]$.¹⁶³ In solution $[\text{Cr}(\text{S}_2\text{CNET}_2)_2]$ is extremely sensitive to air oxidation, converting rapidly to blue $[\text{Cr}(\text{S}_2\text{CNET}_2)_3]$. Very few derivatives have been prepared and there are no crystal structure determinations, thus molecular structure(s) of $[\text{Cr}(\text{S}_2\text{CNR}_2)_2]$ remain unknown, although most likely they are polymeric in the solid state, and tetrahedral in the gas phase or solution. Electrochemical studies of $[\text{Cr}(\text{S}_2\text{CNR}_2)_3]$ show that they undergo a one-electron reduction, with the generated $[\text{Cr}(\text{S}_2\text{CNR}_2)_3]^\bullet$ rapidly losing a dithiocarbamate to give $[\text{Cr}(\text{S}_2\text{CNR}_2)_2]$ ¹⁶⁴ (Fig. 13). However, all attempts to isolate or characterise $[\text{Cr}(\text{S}_2\text{CNR}_2)_2]$ generated in this way have led only to rapid back oxidation and regeneration of $[\text{Cr}(\text{S}_2\text{CNR}_2)_3]$, again highlighting their extreme air-sensitivity.

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

(ii) $\text{M} = \text{Mo}, \text{W}$

We briefly consider the heavier group 6 homologues, $[\text{Mo}(\text{S}_2\text{CNR}_2)_2]$ and $[\text{W}(\text{S}_2\text{CNR}_2)_2]$. The synthesis and X-ray crystal structure of $[\text{Mo}(\text{S}_2\text{CNET}_2)_2]$ has been claimed¹⁶⁶ but is erroneous: the structure presented is that of $[\text{Ni}(\text{S}_2\text{CNET}_2)_2]$ with a misassigned metal atom.¹⁶⁷ Complexes of the stoichiometry $\text{Mo} : \text{dithiocarbamate} 1 : 2$ are known. Thus, reactions of $[\text{Mo}_2(\mu\text{-OAc})_4]$ with four equivalents of dithiocarbamate afford $[\text{Mo}_2(\mu\text{-S}_2\text{CNR}_2)_4]$ as green solids.¹⁶⁸ However, the latter are thermally unstable and upon heating undergo C–S bond scission to yield Mo(V) thiocarboxamide complexes, $[\text{Mo}(\mu\text{-S})(\text{S}_2\text{CNR}_2)(\text{SCNR}_2)]_2$ as shown crystallographically ($\text{R} = i\text{Pr}$).¹⁶⁹ Related W(II) complexes, $[\text{W}(\text{S}_2\text{CNR}_2)_2]$, remain unreported, but both *cis*- $[\text{W}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2]$ and $[\text{W}(\text{CO})_3(\text{S}_2\text{CNR}_2)_2]$ are known¹⁷⁰ as are the corresponding Mo(II) carbonyl complexes.¹⁷¹

(iii) $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$

Bright yellow $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$ 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 $[\text{Mn}(\text{S}_2\text{CNET}_2)_2]$, 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 $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$. 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, $[\text{Mn}(\text{S}_2\text{CNR}_2)_3]$, 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

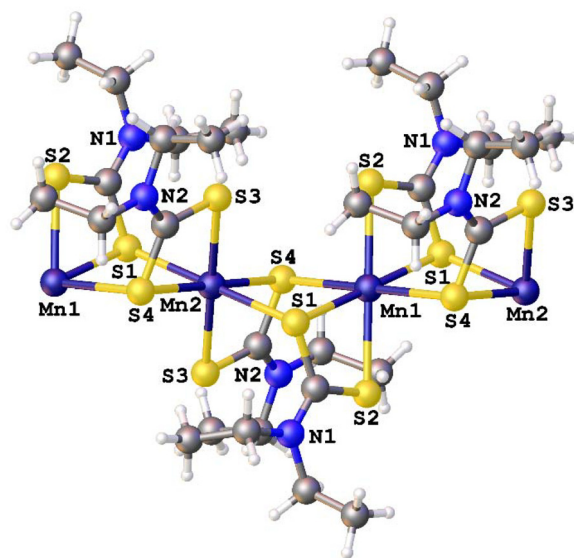


Fig. 14 Part of the polymeric structure of $[\text{Mn}(\text{S}_2\text{CNET}_2)_2]$.¹⁷⁴



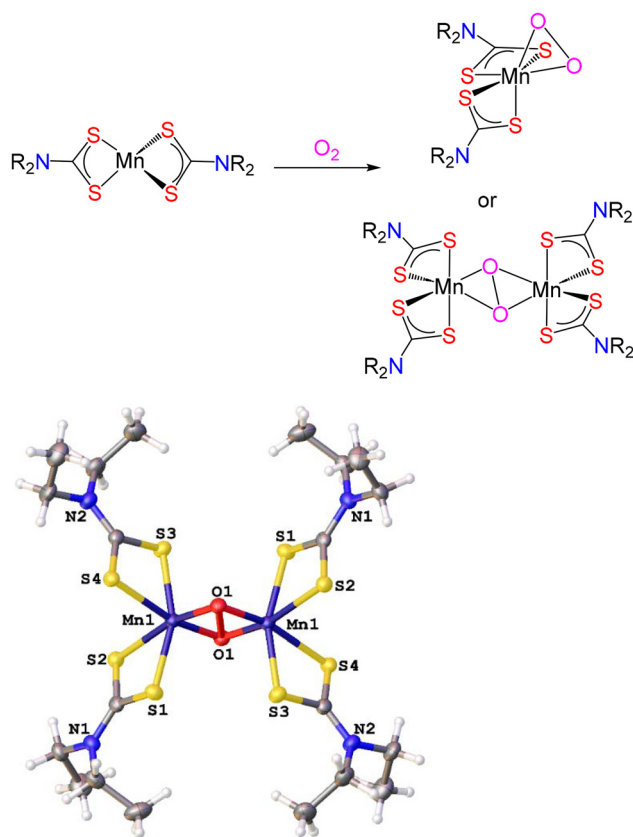


Fig. 15 Oxidation of $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$ with proposed Mn(III) adducts and the molecular structure of $[\text{Mn}_2(\text{S}_2\text{CNEt}_2)_4(\mu\text{-O}_2)]$.^{175,176}

added to Mn(II) salts in water under argon then heavy yellow precipitates result, which are unequivocally $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$. 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 $[\text{Mn}(\text{S}_2\text{CNR}_2)_3]$, 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 $[\text{Mn}(\text{S}_2\text{CNR}_2)_3]$ 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 $[\text{Mn}(\text{S}_2\text{CNR}_2)_3]$ decomposes in a two-step process, the former being associated with loss of a dithiocarbamate and *in situ* formation of $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$, 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).

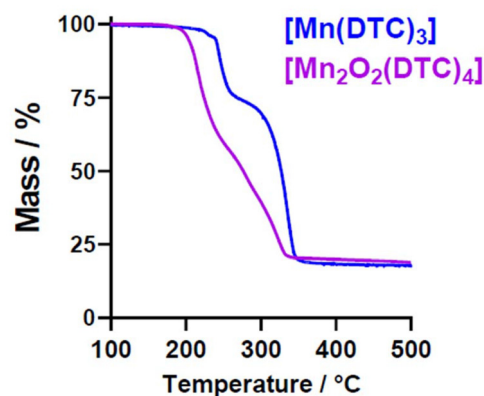


Fig. 16 TGA data for $[\text{Mn}(\text{S}_2\text{CNEt}_2)_3]$ and $[\text{Mn}_2(\text{S}_2\text{CNEt}_2)_4(\mu\text{-O}_2)]$.¹⁷⁶

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 $[\text{Mn}(\text{S}_2\text{CNHC}_2\text{H}_4\text{NHCS}_2) \cdot 2\text{H}_2\text{O}]_n$. Recently a good quality molecular structure of the dimethylformamide (dmf) adduct $[\text{Mn}(\text{S}_2\text{CNHC}_2\text{H}_4\text{NHCS}_2) \cdot 2\text{dmf}]_n$ was reported¹⁸³ (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) $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$

Like their manganese counterparts, $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$ 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 pink¹⁴² or red¹⁸⁴ solids. Crystal structures of two polymorphs of $[\text{Fe}(\text{S}_2\text{CNEt}_2)_2]$ ^{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 $[\text{Fe}$



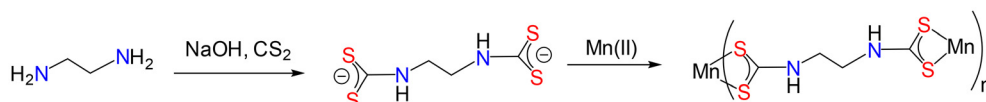


Fig. 17 Formation of Nabem© and reaction with Mn(II) salts to produce Maneb©.

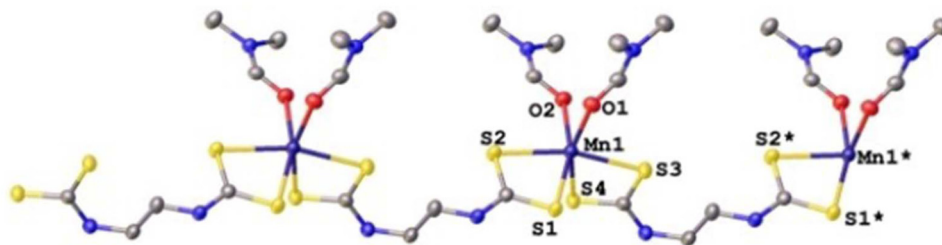


Fig. 18 Part of the polymeric structure of $[\text{Mn}(\text{S}_2\text{CNHC}_2\text{H}_4\text{NCS}_2)\cdot 2\text{dmf}]_n$.¹⁸³

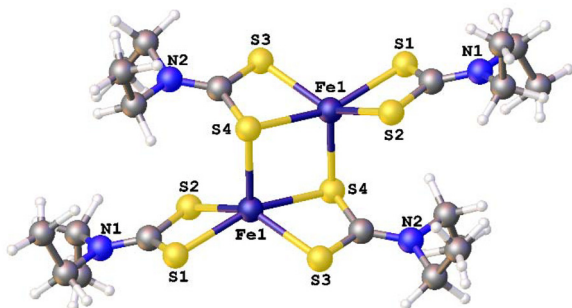


Fig. 19 The molecular structure of $[\text{Fe}(\text{S}_2\text{CNET}_2)_2]_2$.¹⁸⁵

$(\text{S}_2\text{CNR}_2)_2$ 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 $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$ react with excess dithiocarbamate to afford yellow $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]^-$, which are also extremely air sensitive, being rapidly oxidised to brown Fe(III), $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$.¹⁹⁰ Thus, it is most likely that reaction of two equivalents of dithiocarbamate with Fe(II) salts in air simply gives reduced yields of $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$ along with some unreacted Fe(II) salt.

Bis(dithiocarbamate) complexes $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$ 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 $[\text{Fe}(\text{S}_2\text{CNET}_2)_2]$ which co-crystallises with C_{60} ¹⁴⁴ (Fig. 21b). Thus, from aqueous solutions, it may be that a species $[\text{Fe}(\text{S}_2\text{CNR}_2)_2\cdot\text{H}_2\text{O}]$ precipitates out. Interestingly, an NMR spectrum of $[\text{Fe}(\text{S}_2\text{CNC}_4\text{H}_8\text{O})_2\cdot\text{dmf}]$ run in CDCl_3 was found to be identical to that of paramagnetic $[\text{Fe}(\text{S}_2\text{CNC}_4\text{H}_8\text{O})_3]$, 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*- $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2]$ ^{192,193} and NO in $[\text{Fe}(\text{NO})(\text{S}_2\text{CNR}_2)_2]$.^{194,195} Indeed, the binding of NO to $[\text{Fe}(\text{S}_2\text{CNET}_2)_2]$, as determined by the distinctive EPR spectrum of $[\text{Fe}(\text{NO})(\text{S}_2\text{CNET}_2)_2]$, is an accepted way of determining the presence of this important signalling gas.^{196–198} It is noteworthy, however, that reaction of NO with $[\text{Fe}(\text{S}_2\text{CNET}_2)_3]$ also affords $[\text{Fe}(\text{NO})(\text{S}_2\text{CNET}_2)_2]$ (together with thiuram disulfide as a byproduct).¹⁹⁸ Photolysis of $[\text{Fe}(\text{S}_2\text{CNET}_2)_3]$ also results in elimination of thiuram disulfide and formation of $[\text{Fe}(\text{S}_2\text{CNET}_2)_2]$, which can be trapped with bis(diphenylphosphino)ethane (dppe) to afford $[\text{Fe}(\kappa^2\text{-dppe})(\text{S}_2\text{CNET}_2)_2]$.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 $[\text{Fe}(\text{S}_2\text{CN}^i\text{Bu}_2)_3]$ 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*- $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2]$ lose both carbonyls at relatively low temperatures to afford $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$. Thus, $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$, $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$ and *cis*- $[\text{Fe}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2]$ are all effectively equivalents when used as SSPs¹⁹³ thus negating the need to isolate air sensitive $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$.

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

(v) $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$

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



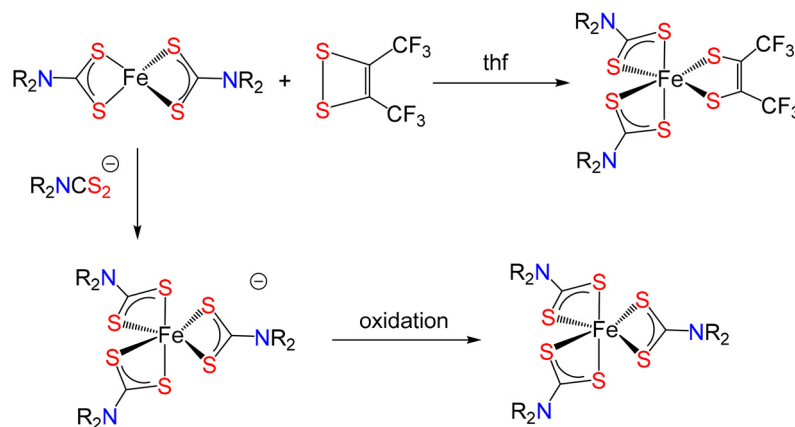


Fig. 20 Reactions of $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$ with a dithietane resulting in oxidation, and addition of further dithiocarbamate followed by oxidation.

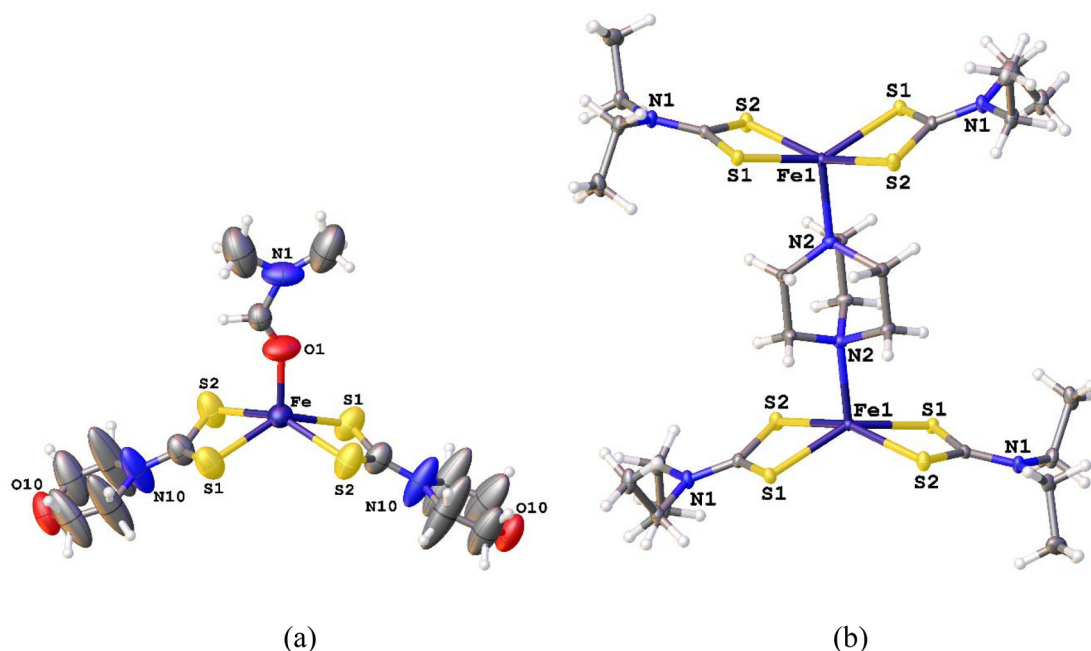


Fig. 21 Molecular structure of (a) $[\text{Fe}(\text{S}_2\text{CNC}_4\text{H}_6\text{O})_2] \cdot \text{dmf}$ ¹⁹¹ and (b) $[\{\text{Fe}(\text{S}_2\text{CNEt}_2)_2\}_2]\text{DABCO}$ as part of a large structure with $\text{C}_{60}\text{-2DABCO}$.¹⁴⁴

It is telling that there are no crystal structures of $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ and examples of authentic syntheses and characterisation are rare. Most authors report the formation of green precipitates from reactions of dithiocarbamate salts with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in air, *i.e.* they actually generate $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$. Recently, Khitrich and co-workers provided some evidence for the formation of $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$,²⁰⁷ suggesting that, provided pH is kept between 6–7, then even in air aqueous solutions of $[\text{CoCl}_2]$ react with two equivalents of NaS_2CNR_2 to afford $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ 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 $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$. 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 $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ and $[\text{Co}(\text{OH})_2]$ (Fig. 22). Clearly more work in this area is warranted.

Electrochemical reduction of $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ leads to dithiocarbamate loss to give $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$, but back oxidation is facile.²⁰⁸ Chemical reduction of $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ 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 $\text{PhI} = \text{NTs}$, the $\text{Co}(\text{II})$ complexes react *via* insertion into the Co–S bonds to afford crystallographically characterised $[\text{Co}\{\text{TsNSC}(\text{NR}_2)\text{SNTs}\}_2]$ ²⁰⁹ (Fig. 23). Thus, it is chemically possible to prepare $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ in organic solvents but oxygen must be rigorously excluded.

We note that there are no authentic examples of $[\text{Rh}(\text{S}_2\text{CNR}_2)_2]$ or $[\text{Ir}(\text{S}_2\text{CNR}_2)_2]$ complexes,^{210,211} all purported



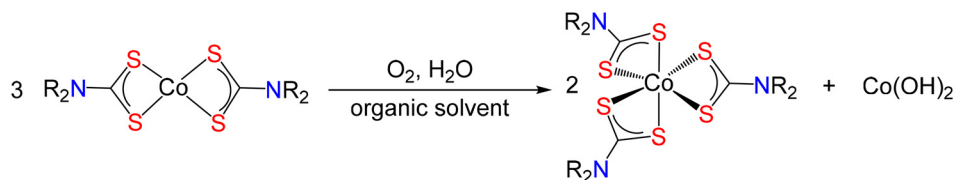


Fig. 22 Proposed decomposition of $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ in organic solvents.²⁰⁷

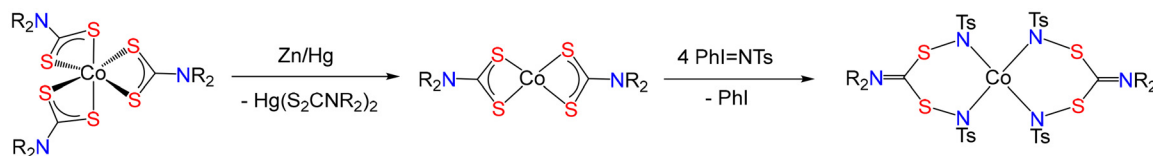


Fig. 23 Reductive generation of $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$ and trapping *via* multiple NTs insertion in the Co–S bonds.

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

5. Structure and stability of dithiocarbamate complexes

(i) $[\text{M}(\text{S}_2\text{CNR}_2)_2]$ ($\text{M} = \text{Mn, Fe, Co}$) are all square planar

In solution or the gas phase, the molecular structures of group 10 bis(dithiocarbamate) complexes and $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]$ are square planar. In the solid state, the 4-coordinate square planar arrangement is maintained for $[\text{M}(\text{S}_2\text{CNR}_2)_2]$ ($\text{M} = \text{Ni, Pd, Pt}$), but the precise metal coordination environment for copper varies with substituents due to secondary $\text{Cu}\cdots\text{S}$ interactions.^{8,13} The solution and gas phase structures of $[\text{M}(\text{S}_2\text{CNR}_2)_2]$ ($\text{M} = \text{Mn, Fe, Co}$) remain unknown, although some authors suggest that all are square planar. This seems highly unlikely for $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$ 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, $[\text{Mn}(\text{S}_2\text{CNET}_2)_2]$ 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 $[\text{Mn}(\text{S}_2\text{CNET}_2)_2]$ and other derivatives show that they adopt a ground state with 5 unpaired electrons.¹⁷² Thus, it seems likely that $[\text{Mn}(\text{S}_2\text{CNR}_2)_2]$ 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, $[\text{Fe}(\text{S}_2\text{CNR}_2)_2]$, with a d^6 electronic configuration have been shown to have 4 unpaired elec-

trons,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 $[\text{Co}(\text{S}_2\text{CNR}_2)_2]$, but they are likely square-planar, as supported by the magnetic susceptibility measurements and DFT calculations.²¹⁸

(ii) Ru(III) complexes $[\text{Ru}(\text{S}_2\text{CNR}_2)_3]$ and $[\text{Ru}(\text{S}_2\text{CNRH})_3]$ are diamagnetic

Iron tris(dialkylDTC) complexes, $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$, have been widely studied as spin crossover complexes as they can adopt either high spin (HS) $^6\text{A}_1$ or low spin (LS) $^2\text{T}_2$ 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, $[\text{Ru}(\text{S}_2\text{CNR}_2)_3]$, although a number of early papers established their fluxional distorted octahedral structures²²³ 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 $[\text{Ru}(\text{S}_2\text{CNR}_2)_3]$, 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 $[\text{Ru}(\text{S}_2\text{CNR}_2)_3]$ and diamagnetic $[\text{Ru}_2(\text{S}_2\text{CNR}_2)_5]^+$ (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, $[\text{Os}$



(S₂CNR₂)₃], are also low spin d⁵ systems that show resonances across a wide chemical shift range in their ¹H 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 (ROCS₂[−]), 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(S₂CNR¹R²)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, K₂[Cr₂O₇], affords a mixture of two Cr(III) products: ring-expanded [Cr(S₂CNR₂)₂(OS₂CNR₂)] as the major component together with [Cr(S₂CNR₂)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 H₂O₂ to [Ru(κ²-2,2'-bipy)(S₂CNMe₂)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(S₂CNEt₂)(OS₂CNEt₂)] was a product of the oxygenation of [Zn(S₂CNEt₂)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(S₂CNR₂)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*-[OsO₂(S₂CNR₂)₂],^{248,249} which show distinctive vibrations at 839 and 888 cm^{−1} in the IR spectrum, being assigned to asymmetric and symmetric *trans*-OsO₂ 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)O₂] moiety is particularly stable, being found for example in complexes such as *trans*-[OsO₂(CO)₄]²⁺ and *trans*-[OsO₂(OH)₄]^{2−}.

(iv) Au(III) complexes, [Au(S₂CNR₂)₂]⁺ and [AuCl₂(S₂CNR₂)], are easily prepared in their pure forms

Gold(III) dithiocarbamate complexes of the type [AuX₂(S₂CNR₂)] (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(S₂CNR₂)_n] with elemental X₂.²⁵¹ This supposedly afforded the Au(III) dithiocarbamate [AuX₂(S₂CNR₂)] 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 [AuX₂(S₂CNR₂)]. 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(S₂CNR₂)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 [AuX₂(S₂CNR₂)] system thoroughly and discovered that the established reactivity is not correct.²⁵² The series of compounds [AuX₂(S₂CNR₂)] where X = halide cannot be isolated as a single species in solution; instead, they exist in an equilibrium with [Au(S₂CNR₂)₂][AuX₄] (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 equi-

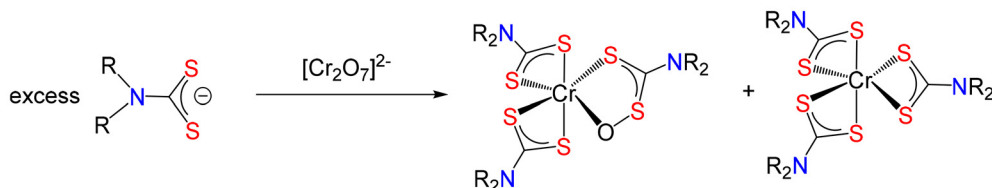


Fig. 24 Cr(III) complexes from reaction of dithiocarbamates and K₂[Cr₂O₇].



rium has always been present even though it had not previously been acknowledged. For example, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of dibenzyl-dithiocarbamate- and methyl-sarcosine-dithiocarbamate-derived $\text{Au}(\text{III})$ 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 $[\text{AuX}_2(\text{S}_2\text{CNR}_2)]$ revealed that the cation $[\text{Au}(\text{S}_2\text{CNR}_2)_2]^+$ was also present in the sample, although it was explained as decomposition in solution.²⁵⁵ A single crystal containing $[\text{AuCl}_2(\text{S}_2\text{CNiPr}_2)]$, two $[\text{Au}(\text{S}_2\text{CNiPr}_2)_2]^+$ cations and two $[\text{ClO}_4]^-$ 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 $[\text{Au}(\text{S}_2\text{CNiPr}_2)_2][\text{AuCl}_4]$ was the majority product could be converted to a mixture where $[\text{AuCl}_2(\text{S}_2\text{CNiPr}_2)]$ was the majority product by refluxing in acetone.²⁵⁷

We note here that it is possible to obtain $[\text{Au}(\text{S}_2\text{CNR}_2)_2]^+$ 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 $[\text{BF}_4]^-$ led to the isolation of $[\text{Au}(\text{S}_2\text{CNR}_2)_2][\text{BF}_4]$ 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 $[\text{AuCl}_4]^-$, the equilibrium restarted.²⁵² In a similar vein, it is possible to isolate $[\text{AuX}_2(\text{S}_2\text{CNR}_2)]$ as a single pure product in solution by avoiding the use of halide ions: stable systems are known to exist for $\text{X} = \text{Me}$, C_6F_5 , mesityl and thiolate, for example.^{258–261}

The above notwithstanding, it is possible to fractionally crystallise $[\text{AuX}_2(\text{S}_2\text{CNR}_2)]$ 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 $[\text{AuX}_2(\text{S}_2\text{CNR}_2)]$ and $[\text{Au}(\text{S}_2\text{CNR}_2)_2][\text{AuX}_4]$, 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} $[\text{M}(\text{S}_2\text{CNHR})_2]$ complexes, but also $[\text{Co}(\text{S}_2\text{CNHR})_3]$ ^{270,271} and $^{99\text{m}}\text{Tc}$ 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 dithiocarbamate (or imidomethanedithiolate) ligand, $\text{S}_2\text{C}=\text{NR}^{2-}$. 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 $[\text{M}(\text{S}_2\text{CNHR})_2]$ and $[\text{M}(\text{S}_2\text{CNHR})_2]$ affords the corresponding dithiocarbamate 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 dithiocarbamate 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 $[\text{M}(\text{S}_2\text{CNHR})_2]$ and $[\text{M}(\text{S}_2\text{CNHR})_2]$ ($\text{M} = \text{Zn}, \text{Cd}$) results in rapid decomposition to give ZnS or CdS nanomaterials.^{266–268} Indeed, this is advantageous, as is the case for $[\text{Ni}(\text{S}_2\text{CNHR})_2]$ 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 $[\text{Fe}(\text{S}_2\text{CNHR})_3]$ ^{279,280} and $[\text{Cu}(\text{S}_2\text{CNHR})_2]$ ^{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 $[\text{Fe}(\text{S}_2\text{CNHR})_3]$ have at best a fleeting stabi-

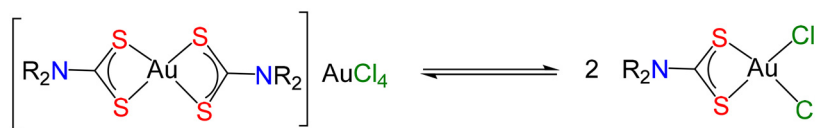


Fig. 25 Equilibrium between $[\text{Au}(\text{S}_2\text{CNR}_2)_2][\text{AuCl}_4]$ and $[\text{AuCl}_2(\text{S}_2\text{CNR}_2)]$.



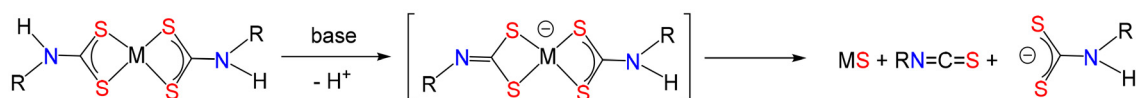


Fig. 26 Base-induced decomposition of $[M(S_2CNHR)_2]$ to afford RNCS and nanoscale metal sulfides.

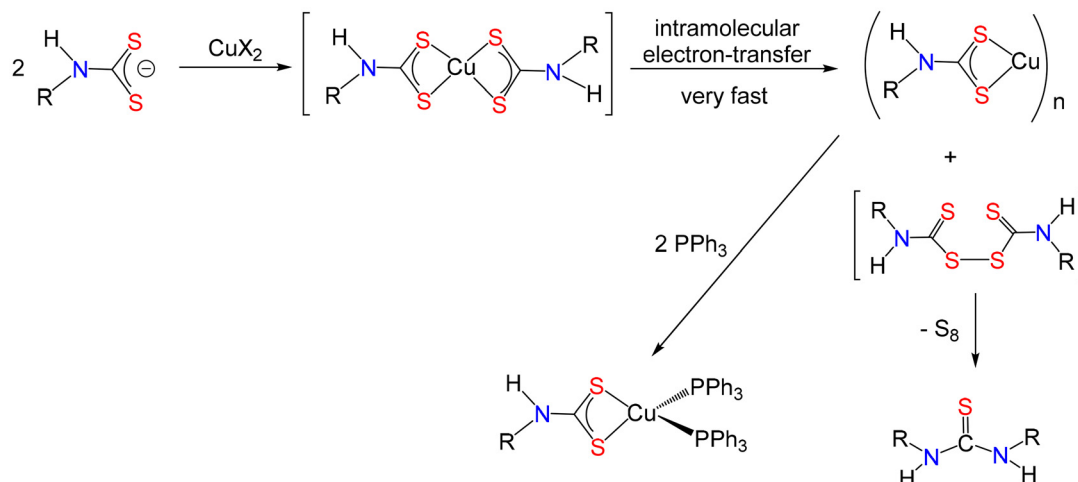


Fig. 27 Formation of $[Cu(S_2CNHR)]_n$ and subsequent reaction with PPh_3 .

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 characterised²⁸⁸ 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 physico-chemical 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 $[Zn(S_2CNMePh)(S_2CNEtPh)(2,2'-bipy)]$ 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and its insensitivity to substituent changes³¹⁷ 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 $\text{M}^{-1} \text{s}^{-1}$ and for Cu(II) slower at *ca.* 10^3 $\text{M}^{-1} \text{s}^{-1}$.^{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 $[\text{Ni}(\text{S}_2\text{CNR}^1)_2](\text{S}_2\text{CNR}^2)_2$,^{318–320} and also between $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ and xanthate complexes, $[\text{Ni}(\text{S}_2\text{COR})_2]$.³²⁵ Most studies support a bimolecular exchange process likely proceeding through a dimeric intermediate, the form of which is common in crystallographic studies of $[\text{Zn}(\text{S}_2\text{CNR}_2)_2]$ and $[\text{Cu}(\text{S}_2\text{CNR}_2)_2]$.⁸ Rapid dithiocarbamate exchange has also been noted at Fe(III)^{326–328} and Hg(II)^{329,330} centres.

For low spin d^6 $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ complexes, the CFSE is so high that exchange rates are slow³³¹ and isolation of mixed-ligand complexes is possible. Thus, addition of a dithiocarbamate salt, $\text{NaS}_2\text{CNR}^1_2$ to $[\text{Co}_2(\text{S}_2\text{CNR}^2_2)_5]^+$ affords a mixture of $[\text{Co}(\text{S}_2\text{CNR}^1_2)(\text{S}_2\text{CNR}^2_2)_2]$ and $[\text{Co}_2(\text{S}_2\text{CNR}^2_2)_3]$ 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 $[\text{Co}(\text{S}_2\text{CNEt}_2)_3]$ and $[\text{Co}(\text{S}_2\text{CN}^i\text{Pr}_2)_3]$ 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 $^{13}\text{C}\{^1\text{H}\}$ 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, $[\text{Co}_2(\text{S}_2\text{CNR}_2)_5]^+$ reacts with a range of nucleophiles to afford $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$ 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 complexes¹⁸⁹ (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 $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$ affords mixed-ligand complexes, examples of which can be crystallographically characterised,

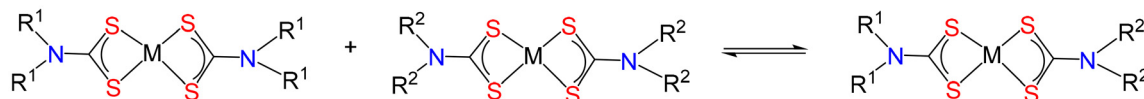


Fig. 28 Equilibrium between homoleptic and mixed ligand bis(dithiocarbamate) complexes.

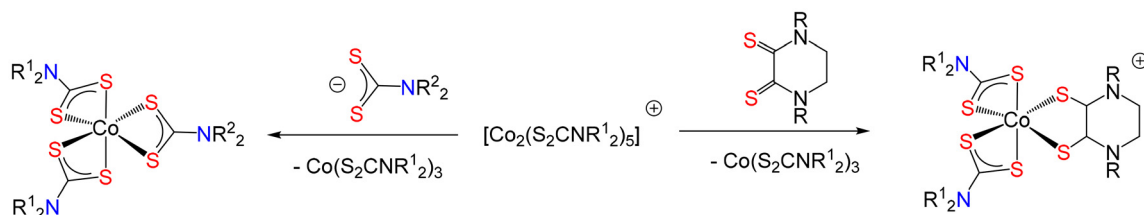


Fig. 29 Synthesis of heteroleptic Co(III) dithiocarbamate complexes.



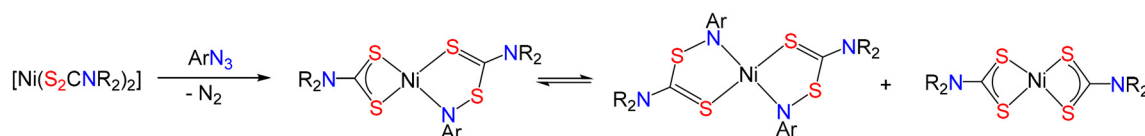


Fig. 30 Formation of mixed-ligand complex in equilibrium with homoleptic complexes.

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 ($\text{M} = \text{Zn}, \text{Cd}$ or Hg) and $\text{M}'\text{Y}_2$ ($\text{M}' = \text{VO}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ or Zn) to a solution of a sodium dithiocarbamate are not heterobimetallic $[\{\text{M}'\text{M}(\text{S}_2\text{CNR}_2)_4\}_n]$ but rather contain a mixture of homonuclear complexes. Likewise, reactions of $\text{Pd}(\text{II})$ salts $[\text{PdCl}_2\text{L}_2]$ ($\text{L} = \text{PhCN}$, $\text{L}_2 = \text{dppe}$) with a series of homoleptic dithiocarbamate complexes affords palladium-dithiocarbamate cations $[\text{Pd}(\text{S}_2\text{CNR}_2)_2\text{L}_2]^+$ with the second metal being incorporated into the counterion.^{341–343} More recently, Torimoto and co-workers added $\text{Na}(\text{S}_2\text{CNET}_2)$ 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 $\text{Cu}_2\text{ZnSnS}_4$ (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 $[\text{Cu}\{\text{S}_2\text{CN}(\text{CH}_2\text{CO}_2\text{H})_2\}_2]$ 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 $[\text{Sn}(\text{S}_2\text{CNET}_2)_2]$ (174 °C) is significantly lower than those of $[\text{Cu}(\text{S}_2\text{CNET}_2)_2]$ (220 °C) and $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ (240 °C), heating this mixture will lead to the premature formation of tin sulfides and hence the tin precursors was replaced by the $\text{Sn}(\text{IV})$ SSPs, $[\text{Sn}(\text{S}_2\text{CNBu}_2)_4]$ ³⁶³ and $[\text{Bu}_2\text{Sn}(\text{S}_2\text{CNBu}_2)_2]$ 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 $\text{Ag}(\text{In}_x\text{Ga}_{1-x})\text{S}_2$ 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



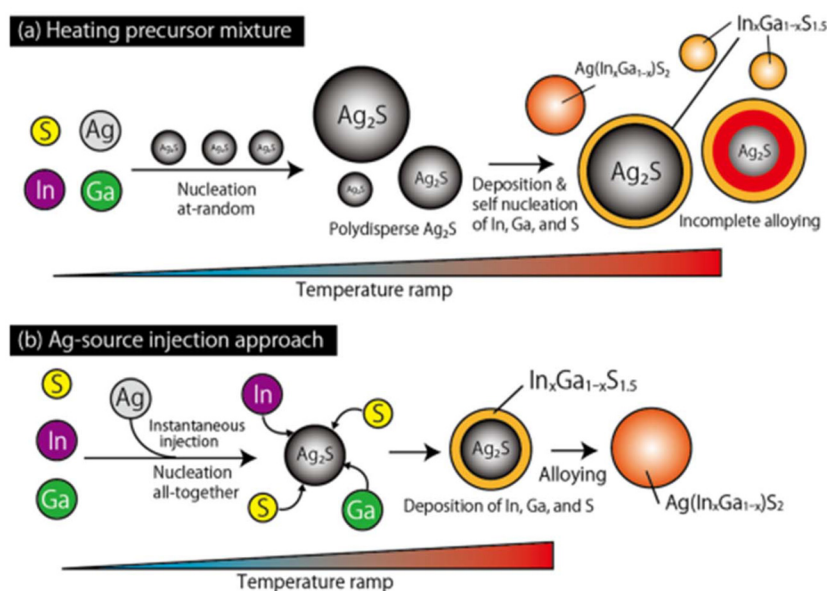


Fig. 31 Schematic illustrations of the synthesis of $\text{Ag}(\text{In}_x\text{Ga}_{1-x})_2\text{S}_2$ quantum dots from (a) heating of the precursor mixture and (b) injecting a silver source into the decomposition mixture.³⁶⁵

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

1891³⁷³ 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 undoubtedly 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.



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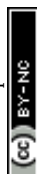
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