A Structural Survey of Poly-Functional Dithiocarbamate Ligands and the Aggregation Patterns They Sustain

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Abstract: An overview is presented of the crystal structures of transition metal, main group element, and lanthanide compounds containing poly-functional dithiocarbamate ligands, namely species containing two or more connected NCS$_2^-$ residues. In all, there are 40 different ligands of this type that have been characterised crystallographically in their heavy-element compounds with up to six NCS$_2^-$ residues; all are bridging. In most cases, the resulting aggregates are zero-dimensional, often di-nuclear, but aggregates of up to 36 metal (gold) atoms are noted. There are smaller numbers of one-, two-, and three-dimensional architectures sustained by poly-functional dithiocarbamate ligands in their respective crystals. The survey highlights the opportunities afforded by this generally under-studied class of ligand.

Keywords: thiolate ligands; dithiocarbamate ligands; coordination polymers; metal clusters; crystal structures

1. Introduction

The facile reaction between a secondary amine and carbon disulphide in the presence of an alkali metal hydroxide or ammonium hydroxide as the base leads to the formation of arguably one of the more important classes of thiolate ligands, the dithiocarbamates, formulated in its simplest form as S$_2$CNR$_2$, for R = alkyl or aryl. While it is not certain when dithiocarbamates were first prepared [1], they have most likely been around for well over 150 years based on the observation that Debus reported the synthesis of dithiocarbamic acids in 1850 [2]; subsequently, Delépine described the synthesis of metal salts of dithiocarbamates in 1907 [3]. The variety of dithiocarbamate anions that can be synthesised is limited by the number of amines available for reaction, and it can extend to primary amines and, relevant to the present survey, molecules bearing two or more amine residues giving rise to poly-functional dithiocarbamate ligands. Being a most prominent ligand in coordination chemistry, over the years, a number of authoritative reviews have summarised advances in the field of dithiocarbamate chemistry and that of their seleno-derivatives [1,4–8], with additional surveys focussing upon aspects of their structural chemistry and modes of supramolecular association in their crystals for specific groups of elements [9–14].

The importance of dithiocarbamate ligands in coordination chemistry notwithstanding, their use in expanding the burgeoning field of metal organic frameworks (MOFs) and coordination polymers is quite plainly lagging compared with, for example, the ubiquitous carboxylates [15]. This is not to suggest there is no role for sulphur in extended framework assemblies. This fact is highlighted in a few very recent reports in the literature exploring the utility of sulphur/sulphur-based ligands in this context. For example, by exploiting band gaps between p- and d-orbitals, two-dimensional metal-organosulphide arrays have long been recognised as important functional materials with applications relating to conductivity, photoluminescence, and ferro-magnetism [16–18]. The authors of a recent study exploring the utility of two-dimensional europium materials featuring Eu–S
bonds as semi-conductors and as precursors for nano-sheets query the apparent lack of sulphur-based materials in this context and conclude this may relate to the perception that metal–sulphur bonds have too much ionic character and are too labile [19]. The present authors also suggest that poor solubility may also be a perceived issue. In terms of specific dithiocarbamate ligands employed in the construction of coordination polymers, perhaps the most relevant recent study relates to a series of heterometallic, platinum(II)/zinc(II) one- and two-dimensional coordination polymers that were synthesised from multi-functional dithiocarbamate ligands featuring both dithiocarbamate and carboxylate residues [20], which were chosen for their complexation ability towards soft platinum(II) and hard zinc(II) centres, respectively. In the context of drug delivery, nanosized thiol-functionalised MOFs have been employed for the transport of the known anti-cancer (leukaemia) and anti-inflammatory drug, 6-mercaptopurine (6-MPH), to cells [21]. Here, 6-MPH was linked, via a disulphide bond, to 2,5-disulfonylterephthalate ligands within a zirconium-based MOF. In the intra-cellular environment, glutathione (GSH), which is present in a higher concentration than in extra-cellular surroundings, reduces the disulphide bond to release 6-MPH in a GSH-responsive drug-delivery strategy that results in a 3-fold efficacy of the drug [21]. In other zirconium-based MOFs, regiospecific and modular substitution in the organic staves of the framework by (thio-ether) sulphur resulted in the formation of boiling water-insensitive materials that could be subjected to controlled, post-synthetic oxidation by hydrogen peroxide [22]; it is noted that (thiophene-)sulphur can play related roles for oxygen reduction in covalent organic frameworks [23]. In one final example highlighting the potential utility of sulphur-modified MOFs, recently, thio-functionalised MOFs have been shown to be effective in bioremediation. Thus, sulphur incorporated into a zinc phosphite framework, through the agency of 2,5-thiophenedicarboxylate linkers, enabled the efficient removal of Hg$^{2+}$ cations from aqueous solution [24].

With the above in mind, it is perhaps surprising that dithiocarbamate ligands do not appear to play a greater or even a prominent role in the construction of MOFs let alone coordination polymers. In this survey, the coordination potential of poly-functional dithiocarbamate ligands, which is defined as molecules having two or more dithiocarbamate residues, that is NCS$^-_2$, available for coordination, is evaluated. The survey is based on the structural data included in the Cambridge Structural Database (CSD) [25]. In all, 102 different crystals have been evaluated, revealing a total of 40 different S$_2$CN-spacer-NCS$_2$ species were identified, and the chemical diagrams for these are given in Figure 1. The full composition of each crystal is given in Table 1 along with their CSD REFCODES. All crystallographic diagrams presented herein are original and were generated with DIAMOND [28] employing data available in the deposited CIFs [25].
Figure 1. Chemical diagrams for poly-functional dithiocarbamate anions L₁ to L₄₀. The asterisk for each of L₂⁹ and L₃₀ indicates the point of attachment.
| Crystal | Formulation | Motif | CSD REFCODE | Ref. |
|---------|-------------|-------|-------------|------|
| 1       | [Mo(=O)₂(L₁)₂] | 0-D/dimer | OFOZIS | [29] |
| 2       | [Ru(dpmm)₂(L₂)₂] | 0-D/dimer | QAVHAX | [30] |
| 3       | [Cp(Ph₃P)Ru₂(L₃)₂] | 0-D/dimer | CULLAW | [31] |
| 4       | [(dpmm)₂Ru₂L₂(Ph₂Ph)₃] | 0-D/dimer | QONVAR | [32] |
| 5       | [(dppe)Ni₂(L₃)₂] | 0-D/dimer | RUDLIM | [33] |
| 6       | [(dppe)Ni₂(L₃)₂] | 0-D/dimer | RUDLOS | [33] |
| 7       | [(dppe)Ni₂(L₃)₂] | 0-D/dimer | ISEWEJ | [34] |
| 8       | Ni₂(L₁)₂, CH₃CN | 0-D/dimer | ELUFLOG | [35] |
| 9       | Ni₂(L₁)₂, 4(H₂O) | 0-D/dimer | QAIFUB | [36] |
| 10      | [(Ph₃P)₂Pd₂(L₂)₂] | 0-D/dimer | KEKKAP | [37] |
| 11      | [(Ph₃P)₂Pd₂(L₂)₂] | 0-D/dimer | KEKKET | [37] |
| 12      | [(Ph₃P)₂Pd₂(L₂)₂] | 0-D/dimer | KEKIX | [37] |
| 13      | [(dppe)Pd₂(L₃)₂] | 0-D/dimer | ISEWIN | [34] |
| 14      | [(dppe)Pd₂(L₃)₂] | 0-D/dimer | RUDLEI | [33] |
| 15      | Pd₂(L₁)₂ | 0-D/dimer | KENYN | [38] |
| 16      | Pd₂(L₁)₂, CHCl₃ | 0-D/dimer | KENYOT | [38] |
| 17      | Pd₂(L₁)₂, 2(CH₃OH), 2.5(H₂O) | 0-D/dimer | QAHGAI | [36] |
| 18      | Pd₂(L₁)₂, 2(CH₃OH) | 0-D/dimer | DIWAN | [39] |
| 19      | [Et₃P]₂Pt₂(L₂) | 2(PF₆) | 0-D/dimer | RUDLAE | [33] |
| 20      | [(Ph₃P)₂Pt₂(L₂)₂] | 2(PF₆) | 0-D/dimer | RUDKUX | [33] |
| 21      | [(Ph₃P)₂Cu₂(L₂)₂] | 2(PF₆) | 0-D/dimer | XUHYAB | [40] |
| 22      | [(Ph₃P)₂CH₂N(Ph)CH₂PPh₂Cu₂L₂(L₁)₂, 2(C₃H₇NO) | 0-D/dimer | ASANUF | [41] |
| 23      | Cu₂(L₁)₂, 2(FeCl₄), 2(C₆H₆) | 0-D/dimer | WOXFAQ | [42] |
| 24      | Cu₂(L₁)₂, CH₂Cl₂ | 0-D/dimer | GUTQIW | [43] |
| 25      | Cu₂(L₁)₂, Re₂O₄ | 0-D/dimer | IDEBIC | [44] |
| 26      | Cu₄(L₁₀)₂ | 0-D/tetramer | GUTQES | [43] |
| 27      | Cu₈(L₁₁)₄, 7(I₃), I, 6(H₂O) | 0-D/decamer | CUPLAA | [45] |
| 28      | (Me₅P)Au₂(L₁) | 0-D/dimer | ISEWUZ | [34] |
| 29      | (Ph₅P)Au₂(L₁) | 2(Ch₂Cl₂), 0.5(CH₃₂CH₂OH) | 0-D/dimer | ISEWOT | [34] |
| 30      | [(Ph₅P)Au₂L₂] | 2(CH₂Cl₂) | 0-D/dimer | YAFMEZ | [46] |
| 31      | [(dppe)Au₂L₂] | 2(PF₆), 1.75(C₄H₁₀O) | 0-D/tetramer | PUCFAV | [47] |
| 32      | Au₆(L₁₂)₁₀, CHCl₃ | 0-D/hexamer | EFARUZ | [48] |
| 33      | Au₈(L¹²)₁₀, unknown solvate | 0-D/octamer | KUNCUT | [49] |
| 34      | Au₈(L¹²)₁₀, unknown solvate | 0-D/octet | KUNDAA | [49] |
| 35      | Au₈(L¹²)₁₀, 3(CHCl₃), 7(H₂O) | 0-D/12-mer | MOLMEX | [50] |
| 36      | Au₁₆(L¹⁵)₁₀, 6(dpmm)₁₀, 8(BF₄), 2(C₂H₃N) | 0-D/16-mer | MUGJUV | [51] |
| 37      | Au₁₆(L¹⁵)₁₀, 8(dpmm)₁₀, 8(PF₆) | 0-D/16-mer | TEBFEM | [52] |
| 38      | Au₁₆(L¹²)₁₀, 10(CHCl₃), 26(H₂O) | 0-D/36-mer | EFAROT | [48] |
| 39      | Zn₂(L₁₂)₁₀, CH₂Cl₂, 2(H₂O) | 0-D/dimer | BAGLIF | [54] |
| 40      | Zn₂(L₁₂)₁₀, CH₂Cl₂, OH, 0.5(H₂O) | 0-D/dimer | QAHGEM | [36] |
| 41      | Zn₂(L₁₂)₁₀(pyridine)₂, 2(C₆H₅N) | 0-D/dimer | FEDDOI | [55] |
| 42      | Zn₂(L₁₂)₁₀(N(CH₂CH₂N)₂) | 0-D/dimer | CUPKUT | [44] |
| 43      | Zn₆(L₁₂)₁₀(pyridine)₆, 7.5(CH₃₂CH₂OH) | 0-D/hexamer | MAKVUP | [56] |
| 44      | Zn₆(L₁₂)₁₀(pyridine)₆, 9(CH₃₂CH₂OH), 10.5(H₂O) | 0-D/hexamer | MAKVUP | [56] |
| 45      | [Zn(L₁₆)₁₀] | 2-D | FUFFAQ | [57] |
| 46      | Cd₆(L₁₆)₁₀(pyridine)₆, 6(CH₃₂CH₂OH), 27(H₂O) | 0-D/hexamer | MAKVUP | [56] |
| 47      | Cd₄(L₁₆)₁₀(pyridine)₆, 15(CH₃₂CH₂OH), 9(H₂O) | 0-D/hexamer | MAKVUP | [56] |
| 48      | (PhHg₂(L₁₂)₁₀, 1.5(EO(EO) | 0-D/dimer | FUPFOM | [58] |
| 49      | (PhHg₂(L₁₂)₁₀ | 0-D/dimer | YOMXJX | [59] |
| 50      | Hg₂(L₁₂)₁₀, 2(CH₂Cl₂) | 0-D/dimer | XOHBAZ | [60] |
| 51      | (Me₅Sn)₂(L₂)₁₀ | 0-D/dimer | BOMCOW | [61] |
| 52      | (Me₅Sn)₂(L₂)₁₀, 2(C₆H₆) | 0-D/dimer | BOMBUB | [61] |
| 53      | (Me₅Sn)₂(L₂)₁₀, 2(CH₂Cl₂) | 0-D/dimer | BOMCAI | [61] |
| 54      | (Me₅Sn)₂(L₂)₁₀, 10(DCCl₃) | 0-D/dimer | SAPSASF | [62] |
| 55      | (Me₅Sn)₂(L₂)₁₀, 2(CHCl₃) | 0-D/dimer | XONHIS | [63] |
Table 1. Cont.

| Crystal | Formulation                                  | Motif | CSD REFCODE | Ref. |
|---------|----------------------------------------------|-------|-------------|------|
| 56      | (Me₂Sn)₂(L₂₆)₂, 2(CH₂Cl₂), 4(C₆H₆)          | 0-D/dimer | BOMCEM     | [61] |
| 57      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂)                 | 0-D/dimer | XONHGOY    | [63] |
| 58      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂)                 | 0-D/dimer | BOMCLOQ    | [61] |
| 59      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂), CH₃CN           | 0-D/dimer | JOVQET     | [64] |
| 60      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂), CH₃CN           | 0-D/dimer | JOVQJX     | [64] |
| 61      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂), CH₃CN           | 0-D/dimer | JOVQOD     | [64] |
| 62      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂), CH₃CN           | 0-D/dimer | JOVQUJ     | [64] |
| 63      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂), CH₃CN           | 0-D/dimer | DORZIT     | [65] |
| 64      | [(nBu)Sn(Ph)Cl]₂, 2(CH₂Cl₂), CH₃CN           | 0-D/dimer | TOHUBP     | [66] |
| 65      | (Ph₂Sn)₂(L₂₄)₂                              | 0-D/dimer | BOMCUC     | [61] |
| 66      | (Ph₂Sn)₂(L₂₄)₂, 6(C₆H₆)                     | 0-D/dimer | SEWGHIM    | [67] |
| 67      | (Me₂SnCl)₂(L₁)                               | 0-D/dimer | UJAFUH     | [68] |
| 68      | (Me₂SnCl)₂(L₂₄)                              | 0-D/dimer | SEWGENI    | [67] |
| 69      | (Me₂SnCl)₂(L₂₄)                              | 0-D/dimer | DOSJAY     | [69] |
| 70      | [(nBu)₂SnCl(L)₂                             | 0-D/dimer | UJAGAO     | [68] |
| 71      | [(nBu)₂SnCl(L)₂                             | 0-D/dimer | POMPOY     | [70] |
| 72      | [(nBu)₂SnCl(L)₂                             | 0-D/dimer | DOSJEC     | [69] |
| 73      | [(nBu)₂SnCl(L)₂                             | 0-D/dimer | PUNDOU     | [71] |
| 74      | (Ph₂SnCl)₂(L₂)                              | 0-D/dimer | QUVJUN     | [72] |
| 75      | (Ph₂SnCl)₂(L₂)                              | 0-D/dimer | POMPUE     | [70] |
| 76      | (Ph₂SnCl)₂(L₂)                              | 0-D/dimer | SANMOL     | [73] |
| 77      | [PhSn(Ph)Cl]₂ (L₂)                          | 0-D/dimer | KOKJIG     | [74] |
| 78      | [PhSn(Ph)Cl]₂ (L₂)                          | 0-D/dimer | KOKJAY     | [74] |
| 79      | (Cy₂Sn)₂(L₂₆)                               | 0-D/dimer | JUMWEW     | [75] |
| 80      | [(PhCH₂)₂Sn]₂(L₂)                           | 0-D/dimer | POMQAL     | [70] |
| 81      | [(2-FC₆H₄)₂Sn]₂(L₂)                         | 0-D/dimer | EXEQAZ     | [76] |
| 82      | [(2-ClC₆H₄)₂Sn]₂(L₂)                        | 0-D/dimer | EXUSEV     | [77] |
| 83      | [(Me₂(Ph)CH₂)₂Sn]₂(L₂)                      | 0-D/dimer | BESKUG     | [78] |
| 84      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | POFVAI     | [79] |
| 85      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | MOTLUC     | [80] |
| 86      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | NORSAP     | [81] |
| 87      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | TOHGEE     | [66] |
| 88      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | POMQEP     | [70] |
| 89      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | YIGHAZ     | [67] |
| 90      | (Ph₂Sn)₂(L₂)                                | 0-D/dimer | SANMIF     | [73] |
| 91      | (Me₂Sn)₂Cl₃(L₂)                             | 0-D/trimer | UJAGES     | [68] |
| 92      | (Me₂Sn)₂Cl₃(L₂)                             | 0-D/trimer | UJAGJW     | [68] |
| 93      | [(tBu)₂SnCl]₃(L₃)                           | 0-D/trimer | UJAGOC     | [68] |
| 94      | [(tBu)₂SnCl]₃(L₃)                           | 0-D/trimer | NOLKUV     | [82] |
| 95      | [(tBu)₂Sn]₂(L₃)                             | 0-D/trimer | NOLLEG     | [82] |
| 96      | [(tBu)₂Sn]₂(L₃)                             | 0-D/trimer | NOLLAC     | [82] |
| 97      | [(H₂O)₂Ce(L²), 2.5(CH₃NO₂), 1.5(H₂O)]ₙ      | 3-D     | PAYPEN     | [83] |
| 98      | [(H₂O)₂Sn(L²), 2.5(CH₃NO₂), 1.5(H₂O)]ₙ      | 3-D     | PAYPIR     | [83] |
| 99      | [(H₂O)₂Eu(L²), 2.5(CH₃NO₂), 1.5(H₂O)]ₙ      | 3-D     | PAYPOX     | [83] |
| 100     | [(H₂O)₂Gd(L²), 2.5(CH₃NO₂), 1.5(H₂O)]ₙ      | 3-D     | PAYPUD     | [83] |
| 101     | [(H₂O)₂Tb(L²), 2.5(CH₃NO₂), 1.5(H₂O)]ₙ      | 3-D     | PAYQAK     | [83] |
| 102     | [(H₂O)₂Nd(L²), 2.5(CH₃NO₂), 1.5(H₂O)]ₙ      | 3-D     | XUPQVW     | [84] |

3. Results
3.1. Coordination Chemistry of a Molybdenum Poly-Dithiocarbamate Complex

In the crystal of 1 [29], originally prepared in connection with studies on steric effects exerted by ligands upon the electrochemistry and kinetics of oxygen atom transfer reactions of relevance to oxomolydenum(VI) enzymes such as sulphite oxidase, two Mo(=O)₂ centres...
are bridged by two $L^1$ dianions to form a di-nuclear molecule, $[\text{Mo(=O)}_2(L^1)]_2$, as shown in Figure 2. The assembly lacks crystallographic symmetry, and the molybdenum(VI) centres exist in distorted octahedral coordination geometries defined by $O_2S_4$-donor sets, as the dithiocarbamate residues are chelating.

![Figure 2](image.png)

**Figure 2.** The di-nuclear molecule of $[\text{Mo(=O)}_2(L^1)]_2$ in the crystal of 1. Colour code and protocols for this and subsequent diagrams: central metal atom, orange; sulphur, yellow; red, oxygen; blue, nitrogen; grey, carbon. Hydrogen atoms have been omitted for clarity.

### 3.2. Coordination Chemistry of Ruthenium Poly-Dithiocarbamate Complexes

There are two structures conforming to the general formula $[\text{Ru}]_2(S_2CN_{\text{sp}}\text{-NCS})_2$ $[\text{Ru}]$. Whereas the structure of di-cationic $[[\text{dppm}]_2\text{Ru}(L^2)]^{2+}$ in 2 $[30]$ lacks crystallographic symmetry, that of neutral $[\text{Cp}(\text{PPh}_3)\text{Ru}_2(L^3)]$ in 3 $[31]$, Figure 3a, is disposed about a centre of inversion; dppm is $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and Cp is $\text{C}_5\text{H}_5^−$. The $L^3$ di-anion in 3 was synthesised by the insertion of phenylisothiocyanate into the silicon–sulphur bond of a silanethiolate precursor complex $[31]$. The coordination geometry for ruthenium in each case is based on a distorted octahedron. In the realisation of the synthetic target towards the formation of hetero-metallic systems, an unusual hetero-metallic species was characterised in 4 $[32]$, namely $[[\text{dppm}]_2\text{Ru}(L^2)\text{Pd}(\text{PPh}_3)_2]^{2+}$. The di-cation was prepared from the reaction of $[\text{Ru}(S_2\text{CNC}_4\text{H}_8\text{NH})_{\text{sp}}\text{-NCS}]_2$ with carbon disulphide under basic conditions followed by the addition of $[\text{PdCl}_2(\text{PPh}_3)_2]$ $[32]$. In the structure, Figure 3b, the $L^2$ di-anion links ruthenium(II) and palladium(II) atoms by chelating each metal centre. The coordination geometry for the ruthenium(II) atom resembles that in 2; the anticipated distorted square-planar geometry is seen for the palladium(II) atom.

![Figure 3](image.png)

**Figure 3.** The di-nuclear molecules of (a) $[[\text{Cp}(\text{PPh}_3)\text{Ru}_2(L^3)]^{2+}$ in 3 and (b) $[[\text{dppm}]_2\text{Ru}(L^2)\text{Pd}(\text{PPh}_3)_2]^{2+}$ in 4. Additional colour code: teal, silicon; pink, phosphorus. The carbon atoms of the Cp, Ph$_3$P, and dppm molecules are illustrated in stick mode.

### 3.3. Coordination Chemistry of Nickel-Triad Poly-Dithiocarbamate Complexes

Poly-nuclear dithiocarbamate complexes are known for each of the nickel-triad elements with those of palladium being structurally characterised the most frequently. Across the triad, regardless of the metal centre, only two distinct structural motifs are observed. There are three di-nuclear nickel(II) complexes formulated as di-cationic $[[\text{Ni}]_2(S_2CN_{\text{sp}}\text{-NCS})_2][\text{Ni}]^{2+}$, each of which is disposed about a centre of inversion. The di-cations found in the crystals of 5–7, respectively, are $[[\text{dppe}]\text{Ni}_2(L^2)]^{2+}$, $[[\text{dpff}]\text{Ni}_2(L^2)]^{2+}$ $[33]$, as illustrated in Figure 4a, and $[[\text{dpff}]\text{Ni}_2(L^1)]^{2+}$ $[34]$, dppe is $\text{Ph}_2\text{P(}\text{CH}_2\text{)}_2\text{PPh}_2$ and
dppf is $\text{Ph}_2\text{P} (\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4) \text{PPPh}_2$; these were prepared from the metathetical reactions of NiCl$_2$(dppe) or NiCl$_2$(dppf) with the potassium salts of L$_1$ or L$_2$, and they were used in the functionalisation of gold nanoparticles by the displacement of a citrate shell [33]. In each case, the P$_2$S$_2$ donor sets in each di-nuclear molecule define a distorted square-planar geometry. The second structural motif is also di-nuclear but charge-neutral and has been characterised in two crystals, namely Ni$_2$(L$_7$)$_2$ (8) [35], as shown in Figure 4b, and Ni$_2$(L$_8$)$_2$ (9) [36]. Here, the $–\text{CS}_2^–$ residues are well-separated and provide bridges to two nickel(II) atoms, each within a square-planar geometry defined by a S$_4$-donor set. In 8, being an early example describing the use of dithiocarbamate ligands for the construction of metal-directed, self-assembled di-metallic cryptands, the di-nuclear molecule is disposed about a centre of inversion and has an open conformation. By contrast, there is no crystallographic symmetry imposed for the di-cation in 9, which has a twisted conformation.

The palladium structures in this section adopt the same structural motifs as for nickel(II). For the motif shown in Figure 4a, two polymorphic forms are known for the $\{[(\text{Ph}_3\text{P})_2\text{Pd}]_2 (L^2)\}^{2+}$ di-cation, one being disposed about a centre of inversion (10) and the other lacking symmetry (11) [37]; $\{[(\text{Ph}_3\text{P})_2\text{Pd}]_2 (L^3)\}^{2+}$ in 12 [37] also lacks symmetry. The primary motivation for the synthesis of 10–12 is related to the study of their potential catalytic activity [37], being evaluated as catalysts for the selective C–H bond functionalisation in the methoxylation of benzo[h]quinoline: the obtained yields of 10-methoxybenzo[h]quinoline were high for each putative catalyst [37]. The same structural motif shown in Figure 4a is found in each of $\{[(\text{dppf})\text{Pd}]_2 (L^4)\}^{2+}$ (13) [34] and $\{[(\text{dppf})\text{Pd}]_2 (L^5)\}^{2+}$ (14) [33]. The structure of each of the next four palladium(II) complexes to be described adopts the di-nuclear structural motif illustrated in Figure 4b. Thus, Pd$_2$(L$_8$)$_2$ (15) [38] is centrosymmetric as for 8. When the same molecule was isolated as its chloroform mono-solvate, in 16 [38], it lacks the crystallographic symmetry of 15, but it adopts essentially the same conformation. The molecular structure of Pd$_2$(L$_7$)$_2$ (17) [36] closely resembles that of the nickel(II) analogue, Ni$_2$(L$_5$)$_2$ (9) [36] and was prepared in a one-pot synthesis from the diamine, carbon disulphide, potassium hydroxide with K$_2$PdCl$_4$ in THF–H$_2$O. A rather more complicated dithiocarbamate di-anion, that is, L$_7$, being constructed about a dihydroxycalix(4)arene residue, is noted in the crystal of 18, leading to a di-nuclear complex formulated as Pd$_2$(L$_7$)$_2$ [39]. Despite the complexity of the formula, the centrosymmetric, di-nuclear molecule resembles the simpler analogues described above.

There are only two platinum(II) complexes with poly-functional dithiocarbamate di-anions, namely, di-cationic and centrosymmetric $\{[(\text{Et}_3\text{P})_2\text{Pt}]_2 (L^2)\}^{2+}$ (19) and $\{[(\text{Ph}_3\text{P})_2\text{Pt}]_2 (L^2)\}^{2+}$ (20) [33], which resemble closely their nickel and palladium congeners.
3.4. Coordination Chemistry of Copper and Gold Poly-Dithiocarbamate Compounds

A total of 18 structures fall into this category, and a fascinating variety of structural motifs are observed for the seven copper-containing and 11 gold-containing structures, there being no examples of silver-containing species. The structural diversity notwithstanding, all aggregation patterns lead to zero-dimensional species.

Five of the copper complexes are di-nuclear and contain copper in varying oxidation states. Two copper(I) centres are linked by a \( \mu_2 \)-bridging \( L^2 \) di-anion in \( ([\text{Ph}_3\text{P}]_2\text{Cu}]_2(L^2) \) \( (21) \) \([40]\), prepared from the reaction of \( (\text{Ph}_3\text{P})_2\text{Cu(NO}_2) \) and \( \text{Na}_2(L^2) \), and these were of interest for their molecular conducting and non-linear optical properties. The centrosymmetric molecule in \( 21 \), shown in Figure 5a, with a \( \text{P}_2\text{S}_2 \)-donor set defining a distorted tetrahedral geometry, is also seen in \( ([\text{Ph}_2\text{PCH}_2\text{N(Ph)CH}_2\text{PPh}_2])\text{Cu}]_2(L^2) \) \( (22) \) \([41]\), having a less commonly observed diphosphane ligand and synthesised for an investigation of its photophysical properties. The next three structures feature well-spaced dithiocarbamate residues enabling the chelation of two copper centres and the formation of metal-containing macrocycles. In the centrosymmetric di-cation, \( ([\text{Cu}_2(L^8)_2])^{2+} \), of crystal \( 23 \) \([42]\), the square-planar copper centres are in the +III oxidation state, providing an exemplary sample of the ability of the dithiocarbamate ligand being able to stabilise high oxidation states owing to a significant contribution of the dithiolate canonical form, that is, \( \text{C=N}^+\text{R}_2 \), to the electronic structure of the dithiocarbamate residue. Indeed, the motivation for the synthesis of \( 23 \) is related to investigations of electrochemical anion sensing by copper-based, redox-active, self-assembled macrocycles. A similar molecular structure is found in neutral \( \text{Cu}_2(L^9)_2 \) \( (24) \) \([43]\), Figure 5b, indicating the presence of copper(II) centres. A more complicated situation occurs in the crystal of mixed-valent \( 25 \) \([44]\), which is the product of the oxidation of \( 24 \) and features large aromatic spacer groups enabling the control of cavity size in the resultant aggregates. The complex is formulated as the catenane, \( ([\text{Cu}_2(L^9)_2])^{2+} \), and lacks crystallographically imposed symmetry; each di-nuclear molecule contains both copper(II) and copper(III) centres. One component of the catenane is shown in Figure 5c, and the mutual interpenetration of two molecules leading to the catenane is represented in Figure 5d.

**Figure 5.** The di-nuclear molecules of (a) \( ([\text{Ph}_2\text{PCH}_2\text{N(Ph)CH}_2\text{PPh}_2])\text{Cu}]_2(L^2) \) in \( 22 \), (b) \( \text{Cu}_2(L^9)_2 \) in \( 24 \) and (c) \( [\text{Cu}_2(L^9)_2]^{3+} \) in \( 25 \). (d) The catenane, \( ([\text{Cu}_2(L^9)_2])^{2+} \), in \( 25 \) in stick form. The carbon atoms of the \( \text{Ph}_2\text{PCH}_2\text{N(Ph)CH}_2\text{PPh}_2 \) molecules are illustrated in stick mode.
When the dithiocarbamate di-anion $L^{10}$ complexes copper(I) centres, a tetra-nuclear aggregate is observed, namely $Cu_4(L^{10})_2$ [43]. As seen from Figure 6a, each $\mu_3$-bridging dithiocarbamate residue links three copper(I) centres whereby one sulphur atom connects to one copper(I) atom and the second sulphur atom connects to two copper(II) atoms. The core of the cluster is a distorted $Cu_4$ tetrahedron disposed about a 2-fold axis of symmetry. The final copper structure to be described reverts to square-planar copper(III) centres in octa-nuclear $[Cu_8(L^{11})_4]^{8+}$ of (27), which were developed for host–guest chemistry [45]. The octacationic species has $S_4$ symmetry and features four resorcarene ligands, each functionalised with four dithiocarbamate residues, with each residue chelating a copper(III) centre, as detailed in Figure 6b. Four such resorcarene ligands are connected into a tetrahedral assembly, being mediated by the eight copper(III) atoms, resulting in the cluster shown in Figure 6c.

Figure 6. (a) Molecular structure of tetra-nuclear $Cu_2(L^{10})_2$ in 26, (b) detail of the tetradentate mode of coordination of the $L^{11}$ di-anion in $[Cu_8(L^{11})_4]^{8+}$ in 27 and (c) molecular structure of octa-nuclear $[Cu_8(L^{11})_4]^{8+}$ in 27.

Of the 11 gold complexes of poly-functional dithiocarbamate ligands, three are di-nuclear, and of these, two are gold(I) mono-phosphane species, $(Me_3PAu)_2(L^1)$ in the crystal of 28 [34], Figure 7a, and $(Ph_3PAu)_2(L^1)$ in 29 [34]; these were prepared by the facile reaction of the phosphanegold(I) chloride precursor with $K_2(L^1)$. Each of these molecules is situated about a centre of inversion, and a monodentate mode of coordination is noted for the dithiocarbamate residue. While the crystallographic symmetry persists in the molecule of $[(Ph_3P)_2AuL_2]$ in 30 [46], as shown in Figure 7b, which was prepared as a synthetic precursor for gold nanoparticles, a distinct coordination geometry is apparent arising from a different mode of coordination by the dithiocarbamate residue. Thus, the gold atom is coordinated by two phosphane-P atoms and is simultaneously chelated by the dithiocarbamate residue, albeit with significantly longer Au–P and Au–S bond lengths compared to those observed in 28 and 29; the $P_2S_2$-donor set in 30 defines a distorted tetrahedral geometry, resembling the nickel(II) and copper(I) congeners, for example 6 and 22, illustrated in Figures 4a and 5a, respectively. Each of the independent
dithiocarbamate residues in the [[(dppf)Au₃]₂(L²)]²⁺ di-cation of 31 [47], prepared by the reaction of (dppf)(AuCl)₂, K₂(L²) and NH₄[PF₆], employs each sulphur atom in a bond to a gold atom. These are further bridged by a dppf molecule to form the tetra-nuclear molecule illustrated in Figure 7c. This arrangement facilitates the formation of aurophilic (Au⋯Au) bonds, which are long known to be prevalent in the supramolecular chemistry of gold complexes [85–87]. Such aurophilic interactions also feature prominently in the subsequent multi-nuclear structures to be described in this section.

![Molecular structures of (a) di-nuclear (Me₃PAu)₂(L¹) in the crystal of 28, (b) di-nuclear [(Ph₃P)₂Au]₂(L²) in 30, (c) tetra-nuclear [(dppf)Au₂]₂(L²) in 31, and (d) hexa-nuclear Au₆(L₁²)₃ in 32, with a simplified version shown in the right-hand side image. When present, the orange dashed lines represent aurophilic (Au⋯Au) bonding interactions.](image)

A hexa-nuclear aggregate, Au₆(L₁²)₃, is evident in the crystal of 32 [48] and is represented in the two views of Figure 7d. As in 31, each sulphur atom of each dithiocarbamate residue links a gold atom so that each L₁² di-anion connects to four gold atoms, and in turn, each gold atom is linked to two L₁² di-anions; the aggregate lacks symmetry. This arrangement leads to the formation of three eight-membered [SCSAu⋯AuSCS] rings, each encompassing an aurophilic interaction. In addition, there are two inter-dimer aurophilic interactions contributing to the stability of the hexamer, and this arrangement facilitates a close to co-planar arrangement of the six gold atoms. The remaining structures contain even more gold atoms in the assembled zero-dimensional aggregates. The motivation for their synthesis was multi-faceted with the primary idea to generate, via a stepwise macro-cyclisation strategy exploiting aurophilic interactions, giant ring systems with potential applications in host–guest chemistry, molecular recognition, and possibly as selective luminescent materials for sensors and OLEDs.
The structures of 33 and 34 [49] have the common feature of having neutral species formulated as \( \text{Au}_8(L^{13})_2 \). The \( L^{13} \) tetra-anion, a tetrakis-dithiocarbamate-calix[4]arene ligand, employs each of the eight sulphur atoms to connect a distinct gold atom. Each of the latter is connected similarly to a second \( L^{13} \) tetra-anion to generate an octa-nuclear capsule or, alternatively, a “gold(I)-containing metallasupramolecular cage”; the aggregate lacks symmetry. Each gold atom is linearly coordinated within an \( S_2 \)-donor set. The capping of pairs of gold atoms results in the formation of four eight-membered \( \{\text{SCSAu} \cdots \text{AuSCS}\} \) rings featuring intramolecular aurophilic interactions, as seen in Figure 8a. There are additional, weaker aurophilic interactions within the cage as well as intermolecular aurophilic interactions; the latter lead to a supramolecular layer in the crystal. Similar “quadruple-stranded helicate dimeric cages” are found for the two independent molecules comprising the asymmetric unit of 34; however, a difference occurs in that the intermolecular aurophilic interactions evident in 33 are absent in the crystal of 34. A similar mode of coordination to that just described is observed for the six \( L^{14} \) ligands in the neutral molecule of \( \text{Au}_{12}(L^{14})_6 \) in the crystal of 35 [50]; the aggregate lacks symmetry, as shown in Figure 8b. The connections between the 12 gold(I) atoms lying in an approximate plane are mediated by aurophilic interactions and the bridging dithiocarbamate residues resides alternatively above and below the best plane through the \( \text{Au}_{12} \) ring.

![Figure 8](image_url)

**Figure 8.** Molecular structures of (a) octa-nuclear \( \text{Au}_8(L^{13})_2 \) in the crystal of 33 and (b) dodeca-nuclear \( \left[\text{Au}_{12}(L^{14})_6\right] \) in 35, with simplified versions shown on the right-hand side of each image.

The basic repeating unit in the 16-gold atom cluster, octa-cationic \( \left[\text{Au}_{16}(L^{15})_4\right]^{8+} \), in the crystal of 36 [51] is a tetramer, that is, di-cationic \( \left[\{(\text{dppm})\text{Au}_2\}_2(L^{15})\right]^{2+} \), whereby each sulphur atom of each dithiocarbamate residue binds a gold atom. The pairs of gold atoms linked by each dithiocarbamate residue are also bridged by a dppm ligand, leading to eight-membered \( \{-\text{PCPAuSCSAu}\} \) rings. As observed above, when this mode of coordination is
apparent, intramolecular aurophilic interactions are formed. In addition, six intermolecular aurophilic interactions are apparent, leading to two curved chains comprising eight gold atoms each, as shown in Figure 9a. A 16-membered gold atom ring is not formed as the separation between two pairs of terminal gold atoms, of approximately 4.40 Å, is considered too long to represent a significant interaction between the atoms. The dithiocarbamate residues around the ring lie on opposite sides, as highlighted in the simplified view of Figure 9a. A similar molecular structure is found in the crystal of 37, featuring \([\text{Au}_{16}(L^2)_4]^{8+}\) octa-cations \(^{52}\), as shown in Figure 9b. The mode of coordination of the \(L^2\) di-anions and their alternating sequence of orientations around the girth of the molecule are as for 36. A difference occurs as in this case; there are aurophilic interactions between each adjacent pair of gold atoms, so the 16 gold atoms define a closed ring with the shape of a bowl, as shown in Figure 9b.

![Figure 9. Molecular structures of (a) \([\text{Au}_{16}(L^{15})_4]^{8+}\) in the crystal of 36 and (b) \([\text{Au}_{16}(L^2)_4]^{8+}\) in 37, with simplified versions shown on the right-hand side.]

The final structure to be described in this section is that of 38, \(\text{Au}_{36}(L^{12})_{18}\) \(^{48}\), which is notable for being a 36 gold atom cluster, as shown in Figure 10. The simplest description of the molecule revolves around a 24-membered ring comprising gold atoms, each forming an aurophilic interaction with its neighbour. Decorating the ring are six additional pairs of gold atoms connected every four \(\text{Au} \cdots \text{Au}\) bonds along the circumference of the ring and orientated perpendicular to the ring so one of the gold atoms is linked to the ring by a pair of aurophilic interactions leading to a \(\cdots \text{Au} \cdots \text{Au} \cdots \text{Au}\) triangle. This can be seen
in the lower views of Figure 10, where the L\textsuperscript{12} dithiocarbamate ligands have been colour-coded to emphasise the Au\textsubscript{6}(L\textsuperscript{12})\textsubscript{3} repeat unit, which resembles a first approximation of the molecular structure observed for the hexa-nuclear Au\textsubscript{6}(L\textsuperscript{12})\textsubscript{3} cluster in the crystal of 32, as shown in Figure 7d.

![Figure 10. Views of the molecular structure of [Au\textsubscript{36}(L\textsuperscript{12})\textsubscript{18}]\textsuperscript{8+} in the crystal of 38 and simplified versions. In the lower views, each L\textsuperscript{12} di-anion has been colour-coded.](image)

3.5. Coordination Chemistry of Zinc-Triad Poly-Dithiocarbamate Compounds

The most numerous examples in this section are species containing zinc with smaller numbers of examples containing cadmium and mercury. There are four instances of di-nuclear zinc(II) aggregates and, curiously, each presents a distinct structural motif, as shown in Figure 11. The original interest in 39 [53] and 40 [54], examples of ditopic poly-ferrocenyl zinc(II)-dithiocarbamate macrocyclic receptors, was to investigate the ability of these substrates to bind and sense, electrochemically, anionic guest species such as isonicotinate and benzoate. Both species were prepared via an in situ route; for example, 39 was prepared from the one-pot reaction of the relevant diamine ligand, potassium hydroxide, carbon disulphide, and zinc(II) acetate hydrate. In the di-nuclear Zn\textsubscript{2}(L\textsuperscript{16})\textsubscript{2} molecule in the crystal of 39 [53], the dithiocarbamate residues of di-anionic L\textsuperscript{16} coordinate in a distinctive fashion, with one chelating one zinc(II) centre and the other residue being bidentate, μ\textsuperscript{2}-bridging. In this way, an eight-membered {–ZnSCS}\textsubscript{2} ring is formed and, being disposed about a centre of inversion, it has an extended chair conformation, as shown in Figure 11a; transannular Zn ⋯ S contacts are noted. The remaining examples, namely Zn\textsubscript{2}(L\textsuperscript{12})\textsubscript{2} in the crystal of 40 [54], Zn\textsubscript{2}(L\textsuperscript{5})\textsubscript{2}(pyridine)\textsubscript{2} in 41 [36], and Zn\textsubscript{2}(L\textsuperscript{9})\textsubscript{2}(N(CH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N) in 42 [55] each have the
common feature that both dithiocarbamate residues are chelating. As shown in Figure 11b, the two zinc(II) centres in 40 are well separated from each other; two independent, non-symmetric molecules comprise the asymmetric unit. The shared feature of the zinc(II) coordination geometries in 39 and 40, each defined by an $S_4$-donor set, is the adoption of distorted tetrahedra. The structural chemistry of mono-functional dithiocarbamate compounds of the zinc-triad elements has been reviewed recently [13], and both dimeric and monomeric structural precedents for each of 39 and 40 are known, but there is a definite predominance of the dimeric form [13]. Isolated monomeric species are generally adopted when the pendant R substituents are large such as in the case when $R = \text{cyclohexyl (Cy)}$, as in $\text{Zn} (\text{S}_2\text{CNCy}_2)_2$ [88], pointing to an influence of steric hindrance upon the adoption of the structural motif adopted in the condensed phase. In the present circumstances, it is noted that there are 14 atoms in the $S\cdots S$ bridge between zinc(II) centres in 39 as opposed to 11 atoms in 40, perhaps suggesting a greater number of atoms offer flexibility in the ligand backbone to enable dimerisation. Similar di-nuclear molecules to that observed in 40 form the core of the structures of 41 [36] and 42 [55] in which complexation to additional donors leads to new structural motifs.

![Figure 11. Molecular structures of (a) $\text{Zn}_2(L^{16})_2$ in the crystal of 39 (dashed lines indicate transannular Zn\cdots S interactions), (b) $\text{Zn}_2(L^{12})_2$ in 40, (c) $\text{Zn}_2(L^{5})_2(\text{pyridine})_2$ in 41 and (d) $\text{Zn}_2(L^{5})_2(\text{N(CH}_2\text{CH}_2)_3\text{N})$ in 42. Additional colour code: green, for acidic hydrogen atoms.](image-url)

In centrosymmetric 41 [36], each zinc(II) atom is additionally coordinated by a pyridine-nitrogen atom with the resulting $NS_4$-donor set being intermediate between distorted trigonal-bipyramidal and square-pyramidal, as shown in Figure 11c. In a sense, an inverse situation is evident in 42, whereby a DABCO (1,4-diazabicyclo(2.2.2)octane) molecule provides an internal bridge between the two zinc(II) centres, so the dithiocarbamate-based macrocycle might be considered a receptor, as shown in Figure 11d. Here, the $NS_4$-donor set defines a coordination geometry approximating a square-pyramid; the di-nuclear molecule is disposed about a centre of inversion, implying the DABCO molecule is disordered. The coordination of the zinc-triad elements by additional donor atoms, such as pyridyl-nitrogen atoms, leads to a very rich diversity of structural outcomes [14], suggesting that further
work in this area is certainly warranted. The next two structures to be discussed are hexa-nuclear and, as for 40–42, feature isolated zinc(II) centres as opposed to the dimers of 39.

The tetrakis dithiocarbamate ligand based on four resorcarene ligands, L11, in neutral Zn6(L11)3 in 43 [45] was observed previously in the [Cu8(L11)4]8+ octa-cation of 27, as shown in Figure 6c. However, in 43, a different arrangement in the hexa-nuclear cluster is noted. Each dithiocarbamate ligand of L11 chelates a zinc atom, and these in turn connect to a second L11 tetra-anion in a cyclic fashion to form the ring shown in the images of Figure 12. The molecule has the shape of a cylinder and is disposed about a crystallographic site of symmetry $\bar{3}$. The NS4-donor set for the independent zinc(II) atom is completed by a pyridine–nitrogen atom and defines a close to square-pyramidal geometry. The structure of Zn6(L17)3 in the crystal of 44 has also been described, where L17 is the N-bound n-butyl analogue of L11 [56]. There is an isomorphous relationship between 43 and 44.

The only coordination polymer is this section, which has only very recently been described, is formed in the crystal of 45, comprising [Zn(L18)]n [57]. The structure is notable for two additional reasons. Firstly, it is the first of two rare examples in the present survey where the dithiocarbamate–nitrogen atom bears a proton and secondly, this compound is long known as an effective fungicide, marketed under the name Zineb® [89]. Indeed, 45 was one of the first industrially relevant fungicides, being commercially available as a fungicide for major crops in Europe and the United States of America during the second half of the 20th century. The asymmetric unit of 45 comprises a zinc(II) atom and two half L18 di-anions, each being disposed about a centre of inversion. The mode of coordination of one of the L18 di-anions is chelating, and that of the other is $\mu_2$-bridging, resembling that seen in [Zn2(L16)2] in 39, as shown in Figure 11a. The result is illustrated in Figure 13, namely, a flat, two-dimensional coordination polymer. The thio–amide–N–H atoms project to either side of the layer, enabling the formation of N–H⋯S hydrogen bonds, leading to a three-dimensional architecture.

![Molecular structure of neutral Zn6(L11)3 in the crystal of 43: plan and side-on views.](image-url)
covered in this survey, that is, of (Me<sub>2</sub>Sn)<sub>2</sub>(L<sub>24</sub>)<sub>2</sub> in (PhHg)<sub>2</sub>(L<sub>19</sub>) [58]; each of the latter is situated about a centre of inversion. As with many of the compounds in this overview, the synthesis and having accessible sites for post-synthetic modification for the optimisation into metallo-supramolecular architectures having cage-like, macrocyclic, or polymeric structures conforming to the (R<sub>2</sub>Sn)<sub>2</sub>(S<sub>2</sub>CN-spacer-NCS<sub>2</sub>)<sub>2</sub> formula is the adoption of a skew-trapezoidal bipyramidal geometry. This arises as the co-planar dithiocarbamate structural motif adopted by mercury(II) mono-functional dithiocarbamate compounds [90].

The common feature of the tin-atom geometries of molecular properties. As with many of the compounds in this overview, the synthesis of (Me<sub>2</sub>Sn)<sub>2</sub>(L<sub>25</sub>)<sub>2</sub> (PhHg)<sub>2</sub>(L<sub>12</sub>) in crystal 48 was to observe differences in the electrochemical and optoelectronic properties with the view of developing novel sensors [58]. Whereas in 48, the phenylmercury species are proximate, occupying syn positions in the molecule, in centrosymmetric 49 [59], the phenylmercury components of (PhHg)<sub>2</sub>(L<sub>19</sub>) are anti, as shown in Figure 14b. Along with solvent, as detailed in Table 1, two independent molecules of Hg<sub>2</sub>(L<sub>20</sub>)<sub>2</sub> comprise the asymmetric unit of 50 [60]; each of the latter is situated about a centre of inversion. One of the di-nuclear molecules is shown in Figure 14c from which it can be seen that one dithiocarbamate residue is chelating while the other is µ<sub>2</sub>-bridging, leading to distorted tetrahedra defined by S<sub>4</sub>-donor sets. This is the common structural motif adopted by mercury(II) mono-functional dithiocarbamate compounds [90].

There are only two cadmium(II) structures to be described—that is, Cd<sub>6</sub>(L<sub>11</sub>)<sub>3</sub> in 46 and Cd<sub>6</sub>(L<sub>17</sub>)<sub>3</sub> in 47 [56], and these are isostructural with their zinc(II) analogues, 44 and 45, with the hexa-nuclear molecule of the former illustrated in Figure 12. In each case, the NS<sub>4</sub>-donor set defines square-pyramidal coordination geometry for the cadmium atom.

The first two of three mercury(II) dithiocarbamate structures to be described in this section are hitherto rare organometallic species. In (PhHg)<sub>2</sub>(L<sub>12</sub>) in crystal 48 [58], as shown in Figure 14a, each dithiocarbamate residue coordinates a mercury(II) atom in a monodentate mode, leading to a di-nuclear molecule; no intramolecular Hg⋯Hg interaction is apparent with the separation being 4.53 Å. Being a heterometallic compound containing both phenylmercury(II) residues and L<sub>12</sub>, bearing ferrocenyl groups, the objective leading to the synthesis of 48 was to observe differences in the electrochemical and optoelectronic properties with the view of developing novel sensors [58]. Whereas in 48, the phenylmercury species are proximate, occupying syn positions in the molecule, in centrosymmetric 49 [59], the phenylmercury components of (PhHg)<sub>2</sub>(L<sub>19</sub>) are anti, as shown in Figure 14b. Along with solvent, as detailed in Table 1, two independent molecules of Hg<sub>2</sub>(L<sub>20</sub>)<sub>2</sub> comprise the asymmetric unit of 50 [60]; each of the latter is situated about a centre of inversion. One of the di-nuclear molecules is shown in Figure 14c from which it can be seen that one dithiocarbamate residue is chelating while the other is µ<sub>2</sub>-bridging, leading to distorted tetrahedra defined by S<sub>4</sub>-donor sets. This is the common structural motif adopted by mercury(II) mono-functional dithiocarbamate compounds [90].
3.6. Coordination Chemistry of Organotin Poly-Dithiocarbamate Compounds

Of all the elements included in this bibliographic review, the most represented are those of tin, with 46 examples. As highlighted in places below, much of the interest in the chemistry of tin dithiocarbamates lies with their various applications [91]. Despite the large number of structures, the number of structural motifs is rather small, being limited to five distinct aggregation patterns. In the following di-functional dithiocarbamate ligands are described before tri-functional analogues, within each category, diorganotin derivatives before triorganotin species, and the discussion is in order of increasing number of resultant zero-dimensional aggregate.

A total of 16 structures conform to the general formula (R₂Sn)₂(S₂CN-spacer-NCS)₂, namely (Me₂Sn)₂L₂ in the crystal of 51 [61], (Me₂Sn)₂(L²²)₂ (52) [61], (Me₂Sn)₂(L²³)₂ (53) [61], (Me₂Sn)₂(L²⁴)₂ (54) [62], (Me₂Sn)₂(L²⁵)₂ (55) [63], (Me₂Sn)₂(L²⁶)₂ (56) [61], [(nBu₂Sn)₂(L²⁷)₂ (57) [63], ([nBu₂Sn]₂(L²¹)₂ (58) [61], ([nBu₂Sn]₂(L²²)₂ (59) [64], ([nBu₂Sn]₂(L²⁸)₂ (60) [64], ([nBu₂Sn]₂(L²⁹)₂ (61) [64], ([nBu₂Sn]₂(L³⁰)₂ (62), [64], ([tBu₂Sn]₂(L¹⁸)₂ (63) [65], [(PhCH₂)₂Sn]₂(L³¹)₂, (64) [66], (Ph₂Sn)₂(L²¹)₂ (65) [61], and (Ph₂Sn)₂(L³²)₂ (66) [67]). The original interest in compounds 51, 52, and, indeed, many of the other oligomeric compounds whose structures will be described herein, related to the desire to incorporate organotin groups, as representatives of organometallic compounds, into metallo-supramolecular architectures having cage-like, macrocyclic, or polymeric structures and having accessible sites for post-synthetic modification for the optimisation of molecular properties. As with many of the compounds in this overview, the synthesis was facile such as in the metathetical reaction leading to 51: the diorganotin dichloride was reacted with K₂L²¹. Additional interest in 59–61 related to their putative anti-cancer potential along with utility as precursors for the deposition of tin sulphide nanomaterials [64], each being classical applications of organotin dithiocarbamates [91]. The screening for anti-cancer potential indicated that the halogen-containing substituents in the dithiocarbamate ligands, as in 59 and 60, increase the cytotoxicity [64]. With the exception of 65, each of the di-nuclear structures in 51–66 is disposed about a centre of inversion; in 51, two independent molecules comprise the asymmetric unit, each being centrosymmetric. A representative molecule, with one of the more unusual dithiocarbamate di-anions covered in this survey, that is, of (Me₂Sn)₂(L²⁴)₂ in (54), is shown in Figure 15a. Another unusual dithiocarbamate di-anion is present in (Me₂Sn)₂(L²⁶)₂ (56), as shown in Figure 15b. The common feature of the tin-atom geometries of 54 and 56, and indeed most of the structures conforming to the (R₂Sn)₂(S₂CN-spacer-NCS)₂ formula is the adoption of a skew-trapezoidal bipyramidal geometry. This arises as the co-planar dithiocarbamate residues coordinate in an asymmetric mode with the two longer Sn–S bonds lying to the same side of the skew-trapezoidal plane through the S₄ atoms. The tin-bound organo substituents lie over the weaker Sn–S bonds. There are three exceptions to this generalisation. In (tBu₂Sn)L¹⁸ in 63, as shown in Figure 15c, one of the dithiocarbamate residues coordinates in a monodentate mode, so the coordination geometry is almost exactly intermediate between square-pyramidal and trigonal-bipyramidal. In each of (Ph₂Sn)₂(L²¹)₂ (65) and (Ph₂Sn)₂(L³¹)₂ in (66), as shown in Figure 15d, more symmetric modes of coordination of the dithiocarbamate residues are apparent, so the cis-C₂S₄ coordination geometries are distorted octahedral. Such perplexing coordination flexibility has been long recognised [91], especially as mono-nuclear diphenyltin bis(dithiocarbamate) molecules which are known to adopt both skew-trapezoidal bipyramidal and octahedral geometries in a ratio of 1:2, and therefore, the study of their structural characteristics continues to attract attention [92].
Despite having a different general formula to the preceding class of compounds, molecules of composition \( (R_2SnX)_2(S_2CN\text{-spacer}\text{-NCS}_2) \) adopt very similar structural motifs in their crystals: \( (Me_2SnCl)_2(L^1) \) in the crystal of 67 [68], \( (Me_2SnCl)_2(L^33) \) [69], \( (Me_2SnCl)_2(L^34) \) [69], \( [(nBu)_2SnCl]_2(L^1) \) [70] [68], \( [(nBu)_2SnCl]_2(L^{32}) \) [71] [70], \( [(nBu)_2SnCl]_2(L^{36}) \) [72] [69], \( [(nBu)_2SnCl]_2(L^{35}) \) [73] [71], \( (Ph_2SnCl)_2(L^2) \) [74] [72], \( (Ph_2SnCl)_2(L^{32}) \) [75] [70], \( (Ph_2SnCl)_2(L^{36}) \) [76] [73], and \( [PhSn(X)CH_2Si(Me)_2C_6H_4C_6H_4Si(Me)_2CH_2Sn(Ph)X](L^2) \) for \( X = Cl \) (77) and \( X = I \) (78) [74]. However, by contrast to the \( (R_2Sn)_2(S_2CN\text{-spacer}\text{-NCS}_2)_2 \) molecules in crystals 51-66, there is a significant diversity of symmetry in the 12 di-nuclear \( (R_2SnX)_2(S_2CN\text{-spacer}\text{-NCS}_2) \) compounds: four have no crystallographically imposed symmetry, that is, 67, Figure 16a, 71, 74, and 75. Compounds 68, as shown in Figure 16b, and 72 are generated by 2-fold symmetry, whereas compounds 69, 70, and 73, as shown in Figure 16c, and 76 are disposed about a centre of inversion; molecules related to 73 attract interest as sensors for anions [71]. In each of 77, as shown in Figure 16d, and 78, where the tin-bound R groups are disparate and one pair of tin-bound R groups is connected, the molecules lack symmetry. The common features of the structures are an asymmetric mode of coordination of the dithiocarbamate residues and the presence of five-coordinate \( R_2S_2X \)-donor sets that are highly distorted from the ideal trigonal-bipyramidal and square-pyramidal extremes. However, owing to the presence of tin-bound electronegative X substituents in the molecular formula, \( (R_2SnX)_2(S_2CN\text{-spacer}\text{-NCS}_2) \), the degree of asymmetry in the mode of coordination is somewhat reduced compared with that in the aforementioned \( (R_2Sn)_2(S_2CN\text{-spacer}\text{-NCS}_2)_2 \) molecules.

**Figure 15.** Molecular structures of (a) \( (Me_2Sn)_2(L^{24})_2 \) in the crystal of 54, (b) \( (Me_2Sn)_2(L^{26})_2 \) in 56, (c) \( [(tBu)_2Sn]_2(L^{18})_2 \) in 63, and (d) \( (Ph_2Sn)_2(L^{32})_2 \) in 66.
compounds showed promising biological activities. Thus, (Ph₃Sn)₂(L₃₆) (§)
ion; in this species compared with diorganotin species. The C₃S-donor sets are based on tetrahedra dentate, reflecting the reduced Lewis acidity of the tin atom centres in the triorganotin coordination of the dithiocarbamate residues is to a first approximation considered mono-
clusion of the dithiocarbamate residues is to a first approximation considered mono-

ded, each hydroxyl–hydrogen atom forms a hydrogen-bond to a thione–sulphur atom
hydrogen atoms afford the opportunity of hydrogen-bond formation in the crystal. In-
examples being (Ph₃Sn)₂(L₃₁) in this category: (Cy₃Sn)₂(L₃₇) in the crystal of
Figure 16. Molecular structures of (a) (Me₂SnCl)₂(L₃) in the crystal of 67, (b) (Me₂SnCl)₂(L₃₃) in 68, (c) [(nBu)₂Sn]₂(L₃₅) in 73, and (d) [PhSn(Cl)CH₂Si(Me)₂C₆H₄C₆H₄Si(Me)₂CH₂Sn(Ph)Cl]L₂ in 77.

The next category of molecular structures also resembles the preceding two classes and conforms to the general formula (R₂SnX)₂(S₂CN-spacer-NCS₂). In all, there are 12 examples in this category: (Cy₃Sn)₂(L₃₇) in the crystal of 79 [75], [(PhCH₂)₂Sn]₂(L₃₂) (80) [70], [(2-FC₆H₄CH₂)₂Sn]₂(L₂) (81) [76], [(2-ClC₆H₄CH₂)₂Sn]₂(L₂) (82) [77], [(Me₂(Ph)CCH₂)₃Sn] in 88 [70], (Ph₃Sn)₂(L₃₅) (83) [78], (Ph₃Sn)₂(L₂) (84) [79], (Ph₃Sn)₂(L₂) (85) [80], (Ph₃Sn)₂(L₂) (86) [81], (Ph₃Sn)₂(L₃₁) (87) [66], (Ph₃Sn)₂(L₃₂) (88) [70], (Ph₃Sn)₂(L₃₃) (89) [67], and (Ph₃Sn)₂(L₃₆) (90) [73]. The molecules are invariably di-nuclear with two representative examples being (Ph₃Sn)₂(L₃₁) in 87 and (Ph₃Sn)₂(L₃₆) in 90, as illustrated in Figure 17. With the exception of 80, 88, and 90, all of the aggregates are disposed about a centre of inversion; in 80, two independent molecules comprise the asymmetric unit. The mode of coordination of the dithiocarbamate residues is to a first approximation considered monodentate, reflecting the reduced Lewis acidity of the tin atom centres in the triorganotin species compared with diorganotin species. The C₃S-donor sets are based on tetrahedra with distortions usually related to the close approach of the non-coordinating thione–sulphur atom. The molecule of 90 is of special interest as the presence of acidic hydroxyl–hydrogen atoms afford the opportunity of hydrogen-bond formation in the crystal. Indeed, each hydroxyl–hydrogen atom forms a hydrogen-bond to a thione–sulphur atom to form a linear, supramolecular tape.

Figure 17. Molecular structures of (a) (Ph₃Sn)₂(L₃₁) in the crystal of 87 and (b) (Ph₃Sn)₂(L₃₆) in 90.

In addition to cytotoxic 59 and 60, [64], several organotin poly-dithiocarbamate compounds showed promising biological activities. Thus, 64 and 87 were tested, in vitro, for fungicidal activity and were found to display good anti-fungal activity towards S. sclerotiorum [66]. Furthermore, 71, 75, 80, and 88 showed promising anti-leishmanial activities [70]. The cytotoxic activities of both 76 and 90 were assayed against two human tumour cell lines; that is, CoLo 205 (colon carcinoma cell) and Bcap37 (mammary tumour cell): the
diorganotin species 76 showed poor cytotoxic activity against the cell lines in comparison to the triorganotin derivative, 90 [73].

The six remaining organotin structures feature tri-functional dithiocarbamate ligands with four of these being (Me₂SnCl)₃(L₃₈) in the crystal of 91, (Me₂SnCl)₃(L₃₉) (92), [(tBu)₂SnCl₂(L₃₈)] in (93) [68], and (Ph₂SnCl)₂(L₃₉) (94) [84]. Specific interest in these compounds, which were synthesised in situ, related to the development of metallo-supramolecular organotin assemblies. None of the tri-nuclear molecules have crystallographically imposed symmetry. As shown in Figure 18a, overall, the molecule in 91 has a bowl-shaped conformation, and this is also evident in each of 93 and 94. By contrast, a somewhat flattened conformation is apparent for 92, as shown in Figure 18b. The C₂ClS₂-donor sets define distorted geometries for the tin atoms as described above, that is, they are intermediate between square-pyramidal and trigonal-bipyramidal.

![Figure 18. Molecular structures of (Me₂SnCl)₃(L₃₈) in the crystal of 91 and (Me₂SnCl)₃(L₃₉) in 92.](image)

The molecules of (Ph₂Sn)₃(L₃₉)₂ in the crystal of 95 and (Ph₂Sn)₃(L₄₀)₂ in 96 [82] are hexa-nuclear. Two views of 95 are given in Figure 19, one slightly off-set from the three-fold axis (the molecule is situated about a crystallographic site of symmetry 32 and the other, side-on). The overall molecule has the shape of a flattened capsule. A similar conformation is noted for (Ph₂Sn)₃(L₄₀)₂ in 96, which has crystallographic 3-fold symmetry. The coordination geometries are distorted octahedral, being based on cis-C₂S₄-donor sets.

![Figure 19. Two views of the molecular structure of (Ph₂Sn)₃(L₃₉)₂ in the crystal of 95.](image)

In should be stressed here that comparisons of key geometric parameters formed by the poly-functional dithiocarbamate ligands with those formed by their mono-functional congeners indicate no definitive trends. This observation is entirely consistent with the results of density functional theory (DFT) calculations which indicate that little or no influence upon the electronic structure of the NCS₂⁻ chromophore is exerted by the nature of the N-bound alkyl substituents [93].

### 3.7. Coordination Chemistry of Lanthanide Poly-Dithiocarbamate Complexes

The motivation for studying lanthanide MOFs, LnMOFs, largely revolves around the luminescent properties of these materials [94] in recognition that such materials are...
relatively unexplored. In this context, a series of tri-valent lanthanides were synthesised, each formulated as \([\{H_3O\}[Ln(L^2)_2] 2.5(CH_3NO_2) 1.5(H_2O)\]_n\) for \(Ln =\) cerium (97), samarium (98), europium (99), gadolinium (100), terbium (101) [83], and neodymium (102) [84] with all six structures being isostructural; the compounds were synthesised from the reactions of \(Ln(NO_3)_3.6H_2O\) (\(Ln = Ce, Sm, Eu, Gd, Tb\) and Nd) with an aqueous solution of \(Na_2[L^2]\). Thus, it is the very last set of structures to be described in this overview that emphasises the potential of poly-functional dithiocarbamate ligands for the construction of MOFs. As shown in Figure 20, the \([Nd(L^2)_2]\]_n\) anions in the crystal of 102 [84] assemble into a three-dimensional framework that defines square channels when viewed down the crystallographic \(c\)-axis; the framework is disordered by symmetry, and the channels are occupied by disordered cations and solvents. The \(L^2\) di-anions are \(\mu_2\)-bridging, chelating two neodymium(III) atoms, each of which is eight-coordinated within a distorted \(S_8\)-cube.

In terms of photoluminescence properties, 98 exhibited well-resolved emission bands in the visible and near-infrared regions in comparison with the other materials [83].

![Figure 20](image-url)

**Figure 20.** A view in projection down the \(c\)-axis of the three-dimensional framework defined by \([Nd(L^2)_2]^−\]_n\) anions in the crystal of 102.

4. Conclusions

This survey of the crystallographic literature has revealed the utility of poly-functional dithiocarbamate ligands in forming multi-nuclear compounds of transition metals, main group elements, and lanthanides. The overwhelming majority of structures are zero-dimensional, ranging from a minimum of two atoms, as is commonly observed, to a maximum 36, the latter in a gold-rich cluster. Rare examples of one-, two-, and three-dimensional aggregation patterns are observed in the crystals. The diversity of poly-functional dithiocarbamate ligands is broad with 40 examples represented herein. All but three of these contain two \(-CS_2^-\) residues with the exceptional examples having three \(-CS_2^-\) residues. In all cases, all \(-CS_2^-\) residues were engaged in coordination to a heavy element. The scope for increasing the range of poly-functional dithiocarbamate ligands with a variety of \(-CS_2^-\) residues is limited only by the number of amine precursor molecules. The synthesis of the compounds is facile, usually relying on simple metathetical
3. Delépine, M. Metallic salts of dithiocarbamic acids; preparation of isothiocyanates in the aliphatic series. Compt. Rend. 1907, 144, 1125–1127.

4. Coucouvanis, D. The chemistry of the dithioacid and 1,1-dithiolate complexes. In Progress in Inorganic Chemistry; Lippard, S.J., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 1970; Volume 12, pp. 295–369. [CrossRef]

5. Eisenberg, R. Structural systematics of 1,1- and 1,2-dithiolato chelates. In Progress in Inorganic Chemistry; Lippard, S.J., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 1970; Volume 12, pp. 295–369. [CrossRef]

6. Coucouvanis, D. The chemistry of the dithioacid and 1,1-dithiolate complexes, 1968–1977. In Progress in Inorganic Chemistry; Lippard, S.J., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 1979; Volume 26, pp. 301–469. [CrossRef]

7. Heard, P.J. Main group dithiocarbamate complexes. In Progress in Inorganic Chemistry; Lippard, K.D., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 2005; Volume 53, pp. 1–69. [CrossRef]

8. Lee, S.M.; Heard, P.J.; Tiekink, E.R.T. Molecular and supramolecular chemistry of mono- and di-selenium analogues of metal dithiocarbamates. Coord. Chem. Rev. 2018, 375, 410–423. [CrossRef]

9. Cox, M.J.; Tiekink, E.R.T. The diverse coordination patterns in the structures of zinc, cadmium and mercury bis(1,1-dithiolates). Rev. Inorg. Chem. 1997, 17, 1–23. [CrossRef]

10. Tiekink, E.R.T. Molecular architecture and supramolecular association in the zinc-triad 1,1-dithiolates. Steric control as a design element in crystal engineering? CrystEngComm 2003, 5, 101–113. [CrossRef]

11. Tiekink, E.R.T. Aggregation patterns in the crystal structures of organometallic Group XV 1,1-dithiolates: The influence of the Lewis acidity of the central atom, metal- and ligand-bound steric bulk, and coordination potential of the 1,1-dithiolate ligands upon supramolecular architecture. CrystEngComm 2006, 8, 104–118. [CrossRef]

12. Tiekink, E.R.T.; Zukerman-Schpector, J. Stereochemical activity of lone pairs of electrons and supramolecular aggregation patterns based on secondary interactions involving tellurium in its 1,1-dithiolate structures. Coord. Chem. Rev. 2010, 254, 46–76. [CrossRef]

13. Tiekink, E.R.T. Exploring the topological landscape exhibited by binary zinc-triad 1,1-dithiolates. Crystals 2018, 8, 292. [CrossRef]

14. Tiekink, E.R.T. Perplexing coordination behaviour of potentially bridging bipyridyl-type ligands in the coordination chemistry of zinc and cadmium 1,1-dithiolate compounds. Crystals 2018, 8, 18. [CrossRef]

15. Ghasempour, H.; Wang, K.-Y.; Powell, J.A.; Karizi, F.Z.; Li, X.-L.; Morsali, A.; Zhou, H.-C. Metal–organic frameworks based on multicarboxylate linkers. Coord. Chem. Rev. 2021, 426, 213542. [CrossRef]

16. Ko, M.; Mendecki, L.; Mirica, K.A. Conductive two-dimensional metal-organic frameworks as multifunctional materials. Chem. Commun. 2018, 54, 7873–7891. [CrossRef] [PubMed]

17. Cave, D.; Gascon, J.-M.; Bond, A.D.; Teat, S.J.; Wood, P.T. Layered metal organosulfides: Hydrothermal synthesis, structure and magnetic behaviour of the spin-canted magnet Co(1,2-(O2C)(SC6H4)). Chem. Commun. 2002, 1050–1051. [CrossRef] [PubMed]

18. Kusamoto, T.; Nishihara, H. Zero-, one- and two-dimensional bis(dithiolato) metal complexes with unique physical and chemical properties. Coord. Chem. Rev. 2019, 380, 419–439. [CrossRef]

19. Zeng, Q.; Wang, L.; Huang, Y.; Zheng, S.-L.; He, Y.; He, J.; Liao, W.-M.; Xu, G.; Zeller, M.; Xu, Z. An air-stable anionic two-dimensional semiconductor metal-thiolate network and its exfoliation into ultrathin few-layer nanosheets. Chem. Commun. 2020, 56, 3645–3648. [CrossRef]
20. Liebing, P.; Witzorke, J.; Oehler, F.; Schmeide, M. Dithiocarbamatoxylylate (DTCC) ligands—Building blocks for hard/soft-heterobimetallic coordination systems. *Inorg. Chem.* **2020**, *59*, 2825–2832. [CrossRef]

21. Gong, M.; Yang, J.; Li, Y.; Gu, J. Glutathione-responsive nanoscale MOFs for effective intracellular delivery of the anticancer drug 6-mercaptopurine. *Chem. Commun.* **2020**, *56*, 6448–6451. [CrossRef]

22. Xian, W.-R.; He, Y.; Diao, Y.; Wong, Y.-L.; Zhou, H.-Q.; Zheng, S.-L.; Liao, W.-M.; Xu, Z.; He, J. A bumper crop of boiling-water-stable metal–organic frameworks from controlled linker sulfuration. *Inorg. Chem.* **2020**, *59*, 7097–7102. [CrossRef]

23. Li, D.; Li, C.; Zhang, L.; Li, H.; Zhu, L.; Yang, D.; Fang, Q.; Qiu, S.; Yao, X. Metal-free thiophene-sulfur covalent organic frameworks: Precise and controllable synthesis of catalytic active sites for oxygen reduction. *J. Am. Chem. Soc.* **2020**, *142*, 8104–8108. [CrossRef]

24. Hsieh, J.; Chen, J.-Y.; Li, H.-Y.; Liu, H.-K.; Tu, H.-L.; Wang, C.-M. A thio-functionalized zinc phosphite with a large-channel framework and enhanced removal ability of mercury ion from aqueous solutions. *Dalton Trans.* **2020**, *49*, 11085–11089. [CrossRef]

25. Taylor, R.; Wood, P.A. A million crystal structures: The whole is greater than the sum of its parts. *Chem. Rev.* **2019**, *119*, 9427–9477. [CrossRef]

26. Bruno, I.J.; Cole, J.C.; Edgington, P.R.; Kessler, M.; Macrae, C.F.; McCabe, P.; Pearson, J.; Taylor, R. New software for searching the Cambridge Structural Database and visualizing crystal structures. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2002**, *58*, 389–397. [CrossRef] [PubMed]

27. Spek, A.L. checkCIF validation ALERTS: What they mean and how to respond. *Acta Crystallogr. Sect. E Crystallogr. Commun.* **2020**, *76*, 1–11. [CrossRef] [PubMed]

28. Brandenburg, K.; Berndt, M. DIAMOND. Version 3.2k; GbR: Bonn, Germany, 2006.

29. Unoura, K.; Abiko, Y.; Yamazaki, A.; Kato, Y.; Coomber, D.C.; Fallon, G.D.; Nakahara, K.; Bond, A.M. Synthesis, structure, and redox behaviour of a novel cis-dioxomolybdenum(VI) dinuclear complex with a quadradentate dithiocarbamate. *Inorg. Chem. Acta* **2002**, *333*, 41–50. [CrossRef]

30. Wilton-Ely, J.D.E.T.; Solanki, D.; Hogarth, G. Multifunctional dithiocarbamates as ligands towards the rational synthesis of polymeric arrays: An example based on a piperazine-derived dithiocarbamate ligand. *Eur. J. Inorg. Chem.* **2005**, *20*, 4027–4030. [CrossRef]

31. Kovács, I.; Lebuis, A.-M.; Shaver, A. Ruthenium-assisted insertion of isothiocyanates into the silicon-sulfur bond: A comparative study on the reactivity of the S-Si and S-H Bonds in CpRu(PPh$_3$)$_2$SX (X = H, SiPr$_3$) complexes. *Organometallics* **2011**, *20*, 35–41. [CrossRef]

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

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

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

35. Beer, P.D.; Berry, N.G.; Cowley, A.R.; Hayes, E.J.; Oates, E.C.; Wong, W.W.H. Metal-directed self-assembly of bimetallic dithiocarbase transition metal complexes and their binding capabilities. *Chem. Commun.* **2003**, *2408–2409*. [CrossRef]

36. Beer, P.D.; Cheetham, A.G.; Drew, M.G.B.; Fox, O.D.; Hayes, E.J.; Rolls, T.D. Pyrrolo-based metallo-macrocycles and cryptands. *Dalton Trans.* **2003**, *603–611*. [CrossRef]

37. Jantan, K.A.; Kwok, C.Y.; Chan, K.W.; Marchio, L.; White, A.J.P.; Deplano, P.; Serpe, A.; Wilton-Ely, J.D.E.T. From recovered metal waste to high-performance palladium catalysts. *Green Chem.* **2017**, *19*, 5846–5853. [CrossRef]

38. Torres-Huerta, A.; Höpfl, H.; Tlahuext, H.; Hernández-Ahuactzi, I.F.; Sánchez, M.; Reyes-Martínez, R.; Morales-Morales, D. Dinuclear macrocyclic palladium dithiocarbamates derived from the homologous series of aliphatic 1,2-diamines (x = 4–10). *Eur. J. Inorg. Chem.* **2013**, *2013*, 61–69. [CrossRef]

39. Webber, P.R.A.; Drew, M.G.B.; Hibbert, R.; Beer, P.D. Transition metal-directed self-assembly of calix[4]arene based dithiocarbamate ligands. *Dalton Trans.* **2004**, *1127–1135*. [CrossRef] [PubMed]

40. Kumar, A.; Mayer-Figge, H.; Sheldrick, W.S.; Singh, N. Synthesis, structure, conductivity, and calculated nonlinear optical properties of two novel bis(triphenylphosphine) copper(II) dithiocarbamates. *Eur. J. Inorg. Chem.* **2009**, *2009*, 2720–2725. [CrossRef]

41. Huang, T.-H.; Yang, H.; Zhu, S.-L.; Zhao, B.; Yang, Y. Synthesis, structures and fluorescent properties of metal complexes based on polyphosphine ligands. *J. Mol. Struct.* **2017**, *1127*, 138–144. [CrossRef]

42. Beer, P.D.; Berry, N.; Drew, M.G.B.; Fox, O.D.; Padilla-Tosta, M.E.; Patell, S. Self-assembled dithiocarbamate-copper(II) macrocycles for electrochemical anion detections. *Chem. Commun.* **2001**, *199–200*. [CrossRef]

43. Cookson, J.; Evans, E.A.L.; Mahler, J.P.; Serpell, C.J.; Paul, R.L.; Cowley, A.R.; Drew, M.G.B.; Beer, P.D. Metal-directed assembly of large dinuclear copper(II) dithiocarbamate macrocyclic complexes. *Inorg. Chem. Acta* **2010**, *363*, 1195–1203. [CrossRef]

44. Padilla-Tosta, M.E.; Fox, O.D.; Drew, M.G.B.; Beer, P.D. Self-assembly of a mixed-valence copper(II)/copper(III) dithiocarbamate catenane. *Angew. Chem., Int. Ed.* **2001**, *40*, 4235–4239. [CrossRef]

45. Fox, O.D.; Drew, M.G.B.; Beer, P.D. Resorcarene-based nanoarchitectures: Metal-directed assembly of a molecular loop and tetrahedron. *Angew. Chem. Int. Ed.* **2000**, *39*, 136–140. [CrossRef]
51. Guzmán-Pécastegui, E.; Zakharov, L.N.; Alvarado-Rodríguez, J.G.; Carnes, M.E.; Johnson, D.W. Synthesis of a self-assembled PhHg(II)/Hg(II) dithiocarbamate macrocycle: Solvent-solvent and solvent-solute interactions in a monomeric and macrocyclic organotin dithiocarbamate derived from 1,10-diaza-18-crown-6 and 4,4'-trimethylenedipiperidine. Cryst. Growth Des. 2008, 8, 19–30. [CrossRef]

52. Lefton, J.B.; Kyle, B.; Pekar, K.B.; Runčevski, T. The crystal structure of Zineb, seventy-five years later. Inorg. Chem. 2011, 50, 637–639. [CrossRef] [PubMed]

53. Lopez-Cardoso, M.; Höpfl, H. Molecular structures and supramolecular association of chlorodiorganotin(IV) complexes with bis- and tris-dithiocarbamate ligand. ARKIVOC 2008, 2008, 89–93. [CrossRef]

54. Guzei, I.A.; Spencer, L.C.; Lillywhite, S.; Darkwa, J. (μ-Piperazine-1,4-dicarbodithioato-κ^3S^1,S^1,S^4,S^4)bis[triphenyolphosphine-κP]gold(II) chloroform disolvate. Acta Crystallogr. Sect. E Crystallogr. Commun. 2011, 67, m1629–m1630. [CrossRef]
70. Ali, S.; Zia-ur-Rehman; Muneeb-ur-Rehman; Khan, I.; Shah, S.N.A.; Ali, R.F.; Shah, A.; Badshah, A.; Akbar, K.; Bélanger-Gariepy, F. New homobimetallic organotin(IV) dithiocarbamates as potent antileishmanial agents. *J. Coord. Chem.* **2014**, *67*, 3414–3430. [CrossRef]

71. Rodriguez-Uribe, N.A.; Claudia-Catalán, M.Á.; Medrano, F.; Pina Luis, G.; Tlahuex, H.; Godoy-Alcántar, C. Anion interaction with homoditopic chlorodiorganotin(IV) dithiocarbamate complexes derived from a naphthalene diimide. A pathway to obtain metallamacrocycles. *Polyhedron* **2020**, *186*, 116415. [CrossRef]

72. Fuentes-Martínez, J.P.; Toledo-Martínez, I.; Román-Bravo, P.; García y García, P.; Godoy-Alcántar, C.; López-Cardoso, M.; Morales-Rojas, H. Diorganotin(IV) dithiocarbamate complexes as chromogenic sensors of anion binding. *Polyhedron* **2009**, *28*, 3953–3966. [CrossRef]

73. Tian, L.; Zheng, X.; Zheng, X.; Sun, Y.; Yan, D.; Tu, L. Synthesis, structure and cytotoxic activity of binuclear phenyltin(IV) complexes with N,N′-bis(2-hydroxybenzyl)-1,2-ethanebis(dithiocarbamate) ligand. *Appl. Organomet. Chem.* **2011**, *25*, 785–790. [CrossRef]

74. Fuentes-Martínez, J.P.; Toledo-Martínez, I.; Román-Bravo, P.; García y García, P.; Godoy-Alcántar, C.; López-Cardoso, M.; Morales-Rojas, H. Diorganotin(IV) dithiocarbamate complexes as chromogenic sensors of anion binding. *Polyhedron* **2009**, *28*, 3953–3966. [CrossRef]

75. Tian, L.; Zheng, X.; Zheng, X.; Sun, Y.; Yan, D.; Tu, L. Synthesis, structure and cytotoxic activity of binuclear phenyltin(IV) complexes with N,N′-bis(2-hydroxybenzyl)-1,2-ethanebis(dithiocarbamate) ligand. *Appl. Organomet. Chem.* **2011**, *25*, 785–790. [CrossRef]

76. Yin, H.-D.; Wang, C.-H.; Xing, Q.-J. Synthesis and molecular structure of binuclear organotin complex bridged by piperazinyl-bidithiocarbamate anion. *Fenxi Ceshi Xuebao* **2004**, *23*, 490–493.

77. Yin, H.; Wang, C. Bis[tri(o-chlorobenzyl)tin(IV)] piperazinylbisdithiocarbamate. *Appl. Organomet. Chem.* **2004**, *18*, 145–146. [CrossRef]

78. Tian, L.; Shang, Z.; Yu, Q.; Li, D.; Yang, G. Bis[tri(2-methyl-2-phenylpropyl)tin]-piperazinylidithiocarbamate. *Appl. Organomet. Chem.* **2004**, *18*, 253–254. [CrossRef]

79. Schmidbaur, H.;叮嘱urib, N.A.; Claudia-Catalán, M.Á.; Medrano, F.; Pina Luis, G.; Tlahuex, H.; Godoy-Alcántar, C. Anion interaction with homoditopic chlorodiorganotin(IV) dithiocarbamate complexes derived from a naphthalene diimide. A pathway to obtain metallamacrocycles. *Polyhedron* **2020**, *186*, 116415. [CrossRef]

80. Yin, H.-D.; Ma, C.-L.; Wang, Y.; Fang, H.-X.; Shao, J.-X. Synthesis and crystal structure of binuclear organotin(IV) complexes [Ph₂Sn(CH₂OH)O₂CC₃H₄CO₂(CH₂OH)SnPh₃]·2CH₂OH and [Ph₂SnS₂CN(CH₂CH₂)₂NCS₂SnPh₃]·2CH₂OH. *Huaxue Xuebao* **2002**, *60*, 897–903.

81. Yin, H.; Deng, B.; Ma, C. Spectroscopic properties and crystal structure of bis[triphenyltin(IV)] piperazine bis(dithiocarbamate). *Fenxi Ceshi Xuebao* **2004**, *23*, 23–26.

82. Reyes-Martínez, R.; García y García, P.; López-Cardoso, M.; Höpf, H.; Tlahuex, H. Self-assembly of diphenyltin(IV) and tri-dithiocarbamate ligands to racemic trinuclear cavitands and capsules. *Dalton Trans.* **2008**, *64*, 4177. [CrossRef] [PubMed]

83. Wang, S.; Xu, J.; Wang, J.; Wang, K.-Y.; Dang, S.; Song, S.; Liu, D.; Wang, C. Luminescence of samarium(III) bis-dithiocarbamate frameworks: Codoped lanthanide emitters that cover visible and near-infrared domains. *J. Mater. Chem. C* **2017**, *5*, 6620–6628. [CrossRef]

84. Xu, J.; Liu, T.; Han, X.; Wang, S.; Liu, D.; Wang, C. Construction of a porous three dimensional rare earth metal–sulfur-ligand open framework. *Chem. Commun.* **2015**, *51*, 15819–15822.

85. Schmidbaur, H. Supramolecular chemistry. Going for gold. *Nature* **2001**, *413*, 31–33. [CrossRef]

86. Schmidbaur, H.; Schier, A. A briefing on aurophilicity. *Chem. Soc. Rev.* **2008**, *37*, 1931–1951. [CrossRef]

87. Tiekink, E.R.T. Supramolecular assembly of molecular gold(I) compounds: An evaluation of the competition and complementarity between aurophilic (Au···Au) and conventional hydrogen bonding interactions. *Coord. Chem. Rev.* **2014**, *275*, 130–153. [CrossRef]

88. Cox, M.J.; Tiekink, E.R.T. Structural features of zinc(II) bis(O-alkylidithiocarbonate) and zinc(II) bis(N,N-dialkyldithiocarbamate) compounds. *Z. Kristallogr.* **1999**, *214*, 184–190. [CrossRef]

89. Guardiola, F.A.; Cuesta, A.; Meseguer, J.; Esteban, M.A. Risks of using antifouling biocides in aquaculture. *Int. J. Mol. Sci.* **2012**, *13*, 1541–1560. [CrossRef] [PubMed]

90. Jotani, M.M.; Tan, Y.S.; Tiekink, E.R.T. Bis[bis(N-2-hydroxyethyl,N-isopropylidithiocarbamato)mercury(II)]₂: Crystal structure and Hirshfeld surface analysis. *Z. Kristallogr. Cryst. Mater.* **2016**, *231*, 403–413. [CrossRef]

91. Tiekink, E.R.T. Tin dithiocarbamates: Applications and structures. *Appl. Organomet. Chem.* **2008**, *22*, 533–550. [CrossRef]

92. Haezam, F.N.; Awang, N.; Kamaludin, N.F.; Jotani, M.M.; Tiekink, E.R.T. (N,N-Dialkyldithiocarbamato-k²S,S')triphenyltin(IV) and bis(N,N-dialkyldithiocarbamato-k²S,S')diphenyltin(IV): Crystal structure, Hirshfeld surface analysis and computational study. *Acta Crystallogr., Sect. E. Crystallogr. Commun.* **2020**, *76*, 167–176. [CrossRef]

93. Tiekink, E.R.T.; Hall, V.J.; Buntine, M.A. An examination of the influence of crystal structure on molecular structure. The crystal and molecular structures of some diorganotinchloro-(N,N-dialkyldithiocarbamato)s, R₂Sn(S₂CN'R²)₂Cl, R = Me, tBu, Ph, Cy; R²′ = (Et)₂, (Et, Cy) and (Cy)₂: A comparison between solid state and theoretical structures. *Z. Kristallogr.* **1999**, *214*, 124–134. [CrossRef]

94. Cui, Y.; Chen, B.; Qian, G. Lanthanide metal-organic frameworks for luminescent sensing and light-emitting applications. *Coord. Chem. Rev.* **2014**, *273–274*, 76–86. [CrossRef]