Exploring the Topological Landscape Exhibited by Binary Zinc-triad 1,1-dithiolates

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Abstract: The crystal chemistry of the zinc-triad binary 1,1-dithiolates, that is, compounds of xanthate \([-\text{S}_2\text{COR}]\), dithiophosphate \([-\text{S}_2\text{P(OR)}_2]\), and dithiocarbamate \([-\text{S}_2\text{CNR}_2]\) ligands, is reviewed. Owing to a wide range of coordination modes that can be adopted by 1,1-dithiolate anions, such as monodentate, chelating, \(\mu_2\)-bridging, \(\mu_3\)-bridging, etc., there exists a rich diversity in supramolecular assemblies for these compounds, including examples of zero-, one-, and two-dimensional architectures. While there are similarities in structural motifs across the series of 1,1-dithiolate ligands, specific architectures are sometimes found, depending on the metal centre and/or on the 1,1-dithiolate ligand. Further, an influence of steric bulk upon supramolecular aggregation is apparent. Thus, bulky \(\text{R}\) groups generally preclude the close approach of molecules in order to reduce steric hindrance and therefore, lead to lower dimensional aggregation patterns. The ligating ability of the 1,1-dithiolate ligands also proves crucial in determining the extent of supramolecular aggregation, in particular for dithiocarbamate species where the relatively greater chelating ability of this ligand reduces the Lewis acidity of the zinc-triad element, which thereby reduces its ability to significantly expand its coordination number. Often, the functionalisation of the organic substituents in the 1,1-dithiolate ligands, for example, by incorporating pyridyl groups, can lead to different supramolecular association patterns. Herein, the diverse assemblies of supramolecular architectures are classified and compared. In all, 27 structurally distinct motifs have been identified.

Keywords: crystal engineering; coordination polymers; structural chemistry; zinc; cadmium; mercury; xanthate; dithiophosphate; dithiocarbamate

1. Introduction

The monofunctional 1,1-dithiolate ligands included in this review are the most well-studied of this class of ligand and have been around for a long time [1]; the chemical structures for the anions covered in this review are illustrated in Figure 1. The first of these, the dithiocarbonate anion, comprises alkyl esters of dithiocarbonic acid, \((\text{RO})\text{C(=S)}\text{SH}\), which are quite unstable, but their alkali metal salts are both stable and easily prepared, usually from the reaction of \(\text{ROH}\), \(\text{CS}_2\), and \(\text{MOH}\). The common name for these anions is “xanthates”. While this term is useful to distinguish these anions from the dithiocarbamates (see below), the name xanthate was actually introduced by the Danish chemist Zeise around 1820. The name is derived from the Greek “xanthos” and was coined in response to the yellow appearance of lead xanthates [2]. Dithiophosphates made their appearance about one century later, being made from the reaction of \(\text{P}_2\text{S}_5\), \(\text{ROH}\), and a base [3]. Particularly pertinent to this review is the fact that zinc(II) dithiophosphates came to the fore in the 1940’s as a versatile class of compounds that were employed in various oils and grease as anti-wear additives, as corrosion inhibitors, and even function as anti-oxidants [4]. The aetiology of the dithiocarbamates is not as well defined [5], as opposed to xanthates and dithiophosphates. Dithiocarbamates have probably been
While this bibliographic review has as its focus the structural characteristics of the binary zinc-triad 1,1-dithiolates, it should be acknowledged that many investigations into these compounds were motivated by a broad range of practical applications such as their use as lubricants, pesticides, in the vulcanisation of rubber, beneficiation reagents of minerals, biological remediation of toxic elements, synthetic precursors for chemical vapour deposition of metal sulphide nanomaterials, and even in medicine as potential therapeutics. In short, the utility of this class of compound has ensured that many X-ray structural studies have been conducted over recent decades. Summaries of the applications and structural motifs/designations are summarised in Table 1.

Figure 1. Chemical diagrams for 1,1-dithiolate ligands covered in this survey: (a) xanthate (O-alkyldithiocarbonate); (b) dithiophosphate; and (c) dithiocarbamate. R, R' = alkyl, aryl.

The interested reader is referred to Delépine, the synthesis of metal salts of dithiocarbamates in 1907 [7].

There are four, six, and 10 zinc, cadmium, and mercury structures to be described in this category.

3. Discussion

3.1. Zinc-Triad Binary Xanthate Structures

There are four, six, and 10 zinc, cadmium, and mercury structures to be described in this category. Starting from zinc, with three distinct structural motifs, it is obvious that an enormous structural diversity is evident among the known crystal structures as, often for these compounds, the xanthate ligand adopts a bidentate bridging mode of coordination. The compounds, coordination donor sets, and structural motifs/designations are summarised in Table 1.
Table 1. Summary of the general features of M(S$_2$COR)$_2$, M = zinc (1–4), cadmium (5–10), and mercury (11–20), structures.

| Compound | R/R′  | Donor set | Motif  | Designation | Ref.  |
|----------|-------|-----------|--------|-------------|-------|
| 1        | Et    | S$_4$     | layer  | A           | [22]  |
| 2        | n-Pr  | S$_4$     | chain  | B           | [23]  |
| 3        | i-Pr  | S$_4$     | tetramer | C         | [24]  |
| 4$^1$    | n-Bu  | S$_4$     | tetramer | C         | [25]  |
| 5        | Me    | S$_6$     | chain  | D           | [26]  |
| 6$^2$    | Et    | S$_4$     | layer  | A           | [27]  |
| 7$^3$    | Et    | S$_4$     | layer  | A           | [28]  |
| 8        | i-Pr  | S$_4$     | layer  | A           | [29,30] |
| 9        | n-Bu  | S$_4$     | layer  | A           | [31]  |
| 10       | CH$_2$CH$_3$OMe | S$_6$  | chain  | D           | [32]  |
| 11       | Me    | S$_3$     | chain  | E           | [33]  |
| 12$^4$   | Et    | S$_4$     | layer  | A           | [34]  |
| 13$^5$   | Et    | S$_4$     | layer  | A           | [35]  |
| 14       | n-Pr  | S$_4$     | layer  | A           | [36]  |
| 15       | i-Pr  | S$_4$     | layer  | F           | [37]  |
| 16       | n-Bu  | S$_4$     | layer  | A           | [38]  |
| 17       | (CH$_2$)$_2$C(H)Me$_2$ | S$_4$  | layer  | A           | [38]  |
| 18       | (CH$_2$)$_2$CMe$_3$  | S$_4$  | layer  | A           | [38]  |
| 19       | Pent  | S$_4$     | layer  | A           | [38]  |
| 20       | C(H)[(CH$_2$)$_2$NCH$_2$Ph] | S$_5$  | chain  | G           | [39]  |

$^1$ Three benzene molecules of solvation per tetramer; $^2$ P$_{2_1}$/c polymorph; $^3$ P$_2_1$ polymorph; $^4$ P$_2_1$ polymorph.

3.1.1. Zinc Xanthates

There are four binary zinc xanthate structures in this category, 1–4 [22–25], and key features of these are summarised in Table 1 along with the other cadmium and mercury structures included in this Section. In 1, that is, with R = Et [22], both xanthate ligands are bidentate, bridging two zinc centres laterally, with the result that a two-dimensional array ensues. As shown in Figure 2a, the layer, with a flat topology, comprises interconnected, 16-membered [$\text{–ZnSCS}$]$^4$ rings. The zinc atom exists within an S$_4$ donor set with each sulphur atom derived from a different xanthate ligand; the S$_4$ coordination geometry approximates a tetrahedron. This structural motif, motif A, is repeated in several cadmium and many mercury analogues (see below). Crucial for the discussion below, is the observation that the ethyl groups are directed above and below the layer.

In what might be thought of as a trivial chemical change, that is, changing R = ethyl in 1 to n-Pr in 2 [23], a major structural change is brought about, which is unprecedented in the analogous chemistry of transition metal xanthates [11–13]. The common features of the two structures are tetrahedral S$_4$ coordination geometries and the formation of 16-membered [$\text{–ZnSCS}$]$^4$ rings. However, in the case of 2, there are both bridging and chelating xanthate ligands. The observed supramolecular chain comprises corner shared 16-membered [$\text{–ZnSCS}$]$^4$ rings, as shown in Figure 2b, and is assigned as structural motif B. Yet another major change in structure is found in isomeric 3, in which the straight chains of 2 are replaced by branched i-Pr groups [24]. As for 1 and 2, S$_4$-tetrahedra and 16-membered [$\text{–ZnSCS}$]$^4$ rings prevail in the structure of 3, but the clear difference is evident from Figure 2c, namely, the structure is an isolated tetramer, motif C. The different structures arise owing to the different ratios of bridging and chelating xanthate ligands: in 1, all ligands are bridging, in 2 the ratio is 2:1, and in 3 there are equal numbers of bridging and chelating xanthate ligands. A qualitative explanation has been offered to rationalise the appearance of the three distinct structural motifs described thus far. This explanation is based on the relative steric bulk of the R groups. In short, the bulkier the R substituent, the less likely it is that supramolecular aggregation will occur. This concept is now well established in the structural chemistry of main group element 1,1-dithiolates [17,40–42] and in the structural chemistry of related organotin carboxylates [43–45], where bulky groups can disrupt
secondary bonding interactions [18,46–48]. Further, it should be stressed that the nature of R, at least that present in the overwhelming majority of zinc-triad xanthate structures, does not exert a significant influence upon the electronic structure of the xanthate anion [49]. In the present series, the relatively bulky i-propyl groups define a three-dimensional exclusion zone around the tetramer in 3, precluding additional bridging. In 2, the exclusion zone defined by the n-propyl groups is two-dimensional so that chains can be formed in the third dimension. Finally, in 1, there is a one-dimensional exclusion zone leading to the layer motif. The final structure in this category, namely [Zn(S$_2$CO-n-Bu)$_2$]$_4$ (4), was isolated as a benzene solvate [25]. The structural motif is as for 1, that is, layer motif, A.

![Figure 2](image_url)

**Figure 2.** Aggregation in the crystals of (a) [Zn(S$_2$COEt)$_2$]$_n$ (1); (b) [Zn(S$_2$CO-n-Pr)$_2$]$_n$ (2); and (c) [Zn(S$_2$CO-i-Pr)$_2$]$_4$ (3). Colour code in this and subsequent diagrams: zinc or cadmium or mercury, orange; sulphur, yellow; oxygen, red, carbon, grey. Non-acidic hydrogen atoms and solvent molecules have been omitted in all diagrams.

3.1.2. Cadmium Xanthates

There are five different xanthate compounds to be described in this Section, 5–10 [26–31], with structures 6 and 7 being polymorphs. The immediate coordination geometry of the cadmium centre in [Cd(S$_2$COMe)$_2$]$_n$ (5) [26] is square-planar, a geometry defined by four sulphur atoms derived from two chelating xanthate ligands, Figure 3a; the cadmium atom lies on a crystallographic centre of inversion. Significant supramolecular aggregation occurs via secondary Cd···S bonding, leading to a 4 + 2 distorted octahedral coordination geometry. It should be noted that the Cd–S bond lengths in the square-plane are not that much shorter than those in the axial positions, that is, 2.64 Å compared with 2.89 Å. The result is the formation of a linear supramolecular chain and is designated as structural motif D. Structures 6–9 uniformly adopt layer motif A in the solid-state, but with minor variations in
the orientations of the alkyl substituents and in the geometric parameters. Structures 6 [27] and 7 [28] have the common composition \([\text{Cd}(S_2\text{COEt})_2]_n\) but, are polymorphs, crystallizing in the \(\text{Pa}\) and \(\text{P2}_1/c\) space groups, respectively. The relationship between the polymorphs is readily seen from the views normal to the layers shown in Figure 3b,c. In 6, the ethyl substituents are orientated to leave voids within the 16-membered \(\{-\text{CdSCS}\}_4\) rings. While this pattern is also apparent in Figure 3c for 7, this only occurs in alternate rows going across the page, and the ethyl groups in the other rows are orientated to block the voids in the rings. This change in symmetry is reflected in the doubling of the relevant crystal axis in 7 compared with 6. In \([\text{Cd}(S_2\text{CO-i-Pr})_2]_n\) (8) [29,30] and \([\text{Cd}(S_2\text{CO-n-Bu})_2]_n\) (9) [31], the same layer motif appears, with that of 8 being the only example with the cadmium atom lying on a special position, in this case a 2-fold axis symmetry, leading to an aesthetically pleasing two-dimensional array, Figure 3d. The last structure in this section, \([\text{Cd}(S_2\text{COCH}_2\text{CH}_2\text{OMe})_2]_n\) (10) [32], closely resembles the structure of 5, being a linear supramolecular polymer with a 4 + 2 coordination geometry for the cadmium atom which lies on a centre of inversion; this is motif D. In this case, there is a greater disparity in the Cd–S bond lengths compared to those in 5, with those in the square-plane of 2.63 and 2.64 Å being significantly shorter than those in the axial positions of 3.02 Å.

**Figure 3.** Aggregation in the crystals of (a) \([\text{Cd}(S_2\text{COMe})_2]_n\) (5); (b) \([\text{Cd}(S_2\text{COEt})_2]_n\) (6); (c) \([\text{Cd}(S_2\text{COEt})_2]_n\) (7); and (d) \([\text{Cd}(S_2\text{CO-i-Pr})_2]_n\) (8).

### 3.1.3. Mercury Xanthates

There are 10 mercury xanthate structures to be described in this Section, 11–20 [33–39], with structures 12 and 13 being polymorphs. A new structural motif, motif E, is realised in the
crystal of [Hg(S$_2$COMe)$_2$]$_n$ (11) [33], being based on a helical chain and propagated by crystallographic 2$_1$ symmetry, Figure 4a. Here, one xanthate ligand is bidentate bridging albeit asymmetrically (Hg–S: 2.38 and 2.92 Å), while the other is monodentate with Hg–S of 2.37 Å. The two sulphur atoms forming the shorter bond lengths are linearly disposed (S–Hg–S is 165°), while the less strongly bound sulphur is in a position orthogonal to the S–Hg–S vector so that the mercury atom has a (planar) T-shaped geometry; the two proximate intra-chain oxygen atoms are disposed well above the HgS$_3$ plane and with Hg⋯O separations of 2×2.93 Å are not considered as significant bonding interactions [33]. Both P$_2_1$ (12) [34] and P$_2_1/c$ (13) [35] polymorphs of [Hg(S$_2$COEt)$_2$]$_n$ have very similar structures and unit cell dimensions, but with the c-axis in 13 being approximately double the a-axis in 12. Each adopts the two-dimensional motif, motif A. The major difference between the polymorphs rests with the symmetry of the two-dimensional grid defined by the mercury atoms, which is marginally squarer in appearance in 12, as judged by the distances between diagonally opposite mercury atoms within the 16-membered [-HgSCS]$_4$ rings, that is, 6.90 and 9.10 Å for 12 and 6.69 and 9.30 Å for 13, indicating that the latter has a more diamond-like appearance. The structures of 12 and 13, with open or accessible voids in the 16-membered rings, resemble the situation in [Zn(S$_2$COEt)$_2$]$_n$ (1) [22] and [Cd(S$_2$COEt)$_2$]$_n$ (6) [27], Pa polymorph, meaning [Cd(S$_2$COEt)$_2$]$_n$, 7 [28], the P$_2_1/c$ polymorph, is the exceptional structure, with half the voids being partially blocked. It is noted that there are no correlations between the space group and congestion about the voids in the 16-membered rings.

![Figure 4](image-url)  
**Figure 4.** Aggregation in the crystals of (a) [Hg(S$_2$COMe)$_2$]$_n$ (11); (b) [Hg(S$_2$CO-i-Pr)$_2$]$_n$ (15); and (c) [Hg(S$_2$COC(H)C(CH$_2$)$_2$NCH$_2$Ph)$_2$]$_n$ (20). Additional colour code: nitrogen, blue.
Two-dimensional arrays are also found in the crystals of \([\text{Hg(S}_2\text{COR)}_2]_n\), for \(R = \text{n-Pr (14)}\) \([36]\), \(\text{i-Pr (15)}\) \([37]\), \(\text{n-Bu (16)}\), \(\text{CH}_2\text{CH}_2\text{C(H)Me}_2 (17)\), \(\text{CH}_2\text{CH}_2\text{CMe}_3 (18)\), and \(\text{Pentyl} (19)\) \([38]\). With the exception of 15, the structures adopt the common motif A and with obvious voids in the structure when viewed normal to the plane of the array; congestion obviously increases with the size of the \(R\) substituent, especially in 17 and 18. A new structural motif is found for \([\text{Hg(S}_2\text{CO-i-Pr)}_2]_n\) (15) \([37]\), designated as F. This motif has features found for the majority of the zinc-triad binary xanthates in that one of the two independent mercury atoms is tetrahedrally coordinated by four sulphur atoms derived from four bridging xanthate ligands, that is, characteristic of motif A. By contrast, the second independent mercury atom has its tetrahedral \(S_4\) donor set defined by a chelating xanthate ligand, as well as two sulphur atoms derived from two bridging xanthates, that is, reminiscent of the zinc xanthate motifs B and C (see above). As all bridging xanthate ligands extend laterally, the overall structure is two-dimensional, as shown in Figure 4b.

The final structure to be described in this section has a non-conventional oxygen-bound substituent, that is, 1-benzylpiperidin-4-yl to yield \([\text{Hg(S}_2\text{COC(H)[(CH}_2]_2\text{NCH}_2\text{Ph)}_2]_n}\) (20) \([39]\). In the crystal, this is a coordination polymer with five-coordinate mercury atoms, Figure 4c. Thus, the mercury atom is coordinated by two chelating xanthate ligands, one of which simultaneously bridges a symmetry-related mercury atom to generate the chain. A measure of the nature of the coordination geometry for five-coordinate systems is the value of \(\tau\), which is 0.0 for an ideal square-pyramidal geometry and 1.0 for an ideal trigonal-pyramid \([50]\). In 20, the \(S_5\) coordination geometry approximates a square-pyramid with \(\tau = 0.20\). In this description, the less tightly bound sulphur atom involved in forming the bridge occupies the apical position. In acknowledgement of the different coordination mode/geometry of the linear coordination polymer in 20, this structure is assigned as motif G.

### 3.2. Zinc-Triad Binary Dithiophosphate Structures

The zinc-triad binary dithiophosphates comprise the smallest number of structures of the 1,1-dithiolates surveyed herein. Nevertheless, new and unprecedented structural motifs occur, with the common feature of all motifs being an \(S_4\) donor set for the central element; all structures crystallised solvent-free. Data for the 15 zinc-triad binary dithiophosphate structures, 21–35 \([51–63]\), discussed in this section are presented in Table 2.

#### Table 2. Summary of the general features of \(M[S_2P(OR)_2]\), \(M = \text{zinc (21–24), cadmium (25–31), and mercury (32–35)}\), structures.

| Compound | \(R\) | Donor set | Motif | Designation | Ref. |
|----------|-----|----------|-------|-------------|-----|
| 21       | Me  | \(S_4\)  | H     | chain       | [51]|
| 22       | i-Pr| \(S_4\)  | I     | dimer       | [52]|
| 23       | i-Bu| \(S_4\)  | I     | dimer       | [53]|
| 24       | Cy  | \(S_4\)  | I     | dimer       | [54]|
| 25       | Me  | \(S_4\)  | J     | chain       | [55]|
| 26       | n-Pr| \(S_4\)  | J     | chain       | [56]|
| 27       | i-Pr| \(S_4\)  | I     | dimer       | [52]|
| 28       | n-Bu| \(S_4\)  | J     | chain       | [56]|
| 29       | i-Bu| \(S_4\)  | J     | chain       | [57]|
| 30       | s-Bu| \(S_4\)  | I     | dimer       | [58]|
| 31       | Cy  | \(S_4\)  | K     | dimer       | [59]|
| 32       | Me  | \(S_4\)  | A     | layer       | [60]|
| 33 \(^1\) | i-Pr| \(S_4\)  | L     | chain       | [61]|
| 34 \(^2\) | i-Pr| \(S_4\)  | L     | chain       | [62]|
| 35       | c-Pentyl| \(S_4\)  | L     | chain       | [63]|

\(^1\) \(C_2/c\) polymorph; \(^2\) \(P_2_1/c\) polymorph.
3.2.1. Zinc Dithiophosphates

Of the four known zinc dithiophosphates, 21–24 [51–54], two distinct and thus far, unprecedented structural motifs, are observed. For the structure with the smallest R substituent, \([\text{Zn}[\text{S}_2\text{P(OMe)}_2]_2]_n\) (21) [51], a zig-zag supramolecular chain is formed in the crystal as the result of bidentate bridging dithiophosphate ligands propagated by glide symmetry matched by equal numbers of chelating ligands, Figure 5a. This new motif is designated motif H. The second motif for zinc dithiophosphates is found for each of \([\text{Zn}[\text{S}_2\text{P(O-i-Pr)}_2]_2]_2\) (22) [52], \([\text{Zn}[\text{S}_2\text{P(O-i-Bu)}_2]_2]_2\) (23) [53], and \([\text{Zn}[\text{S}_2\text{P(OCy)}_2]_2]_2\) (24) [54], and also features equal numbers of bridging and chelating ligands, but in this case leading to a dimeric aggregate, as illustrated for 24 in Figure 5b. The aggregates in 22 and 24 have crystallographic 2-fold symmetry while that in 23 approximates 2-fold symmetry. This motif is assigned as motif I. As indicated below, many of the zinc-triad dithiocarbamates adopt a very similar motif, but often these feature quite significant transannular M···S interactions and are centrosymmetric. In motif I, the zinc atom coordination geometries are distorted tetrahedrally based on S₄ donor sets, indicating the absence of transannular Zn···S interactions.

![Figure 5. Aggregation in the crystals of (a) \([\text{Zn}[\text{S}_2\text{P(OMe)}_2]_2]_n\) (21) and (b) \([\text{Zn}[\text{S}_2\text{P(OCy)}_2]_2]_2\) (24). Additional colour code: phosphorus, pink.](image)

3.2.2. Cadmium Dithiophosphates

There are seven structures in this category and these adopt two distinct structural motifs in the solid-state, one of which is new. The new motif, J, is found in the crystals of four compounds, namely \([\text{Cd}[\text{S}_2\text{P(OR)}_2]_2]_n\) for R = Me (25) [55], Figure 6a; n-Pr (26) [56]; n-Bu (28) [56]; and i-Bu (29) [57]. Here, all dithiophosphate ligands are bidentate bridging, leading to eight-membered \(-\text{SPSCd}_2\) rings that are linked at the cadmium atom to form a twisted chain; the chain in 25 has crystallographic 2-fold symmetry. The eight-membered ring in motif J has the form of a boat with two sulphur atoms above and two below the plane through the Cd₂P₂ atoms. The remaining three structures, \([\text{Cd}[\text{S}_2\text{P(OR)}_2]_2]_2\) for R = i-Pr (27) [52]; s-Bu (30) [58], Figure 6b; and Cy (31) [59], adopt motif I. A distinguishing feature of 31 is that the dimeric aggregate is disposed about a centre of inversion as opposed to 2-fold symmetry for 27 and 30. In order to distinguish between the two symmetries for the dimer, dimeric aggregates with 2-fold symmetry, approximate or crystallographically-imposed, are designated as I, while those disposed about a centre of inversion or close to this are designated as K. Finally, in terms of the two structural motifs adopted by cadmium dithiophosphates, that is, to a first approximation dimeric or polymeric, it is noted that for the three derivatives with branching at the alpha-carbon atom, the dimer form is adopted, again suggesting a significant steric influence in determining the ultimate motif found in the crystal.
3.2.3. Mercury Dithiophosphates

There are four structures to be described in this section, but only three compounds as a pair are polymorphic. The structure of [Hg(S₂P(O-i-Pr)₂)₂]ₙ (32) [60] is a two-dimensional layer as all dithiophosphate ligands are bidentate bridging. As seen in Figure 7a, the resemblance between this structure, with edge-shared 16-membered [-HgSPS]₄ rings, and those of many of the zinc-triad xanthates is obvious and accordingly, this is an example of motif A. The three remaining examples, that is, polymorphic [Hg(S₂P(O-i-Pr)₂)₂]ₙ (33) [61] and (34) [62], adopting C2/c and P2₁/c space groups, respectively, and [Hg(S₂P(O-c-Pentyl)₂]ₙ (35) [63], Figure 7b, also adopt a previously described structural motif. Thus, linear chains arising from equal numbers of chelating and bridging dithiophosphate ligands are found, akin to motif H. However, in motif H, the chains have a zig-zag topology, whereas in 33–35, a helical topology is evident as the coordination polymers are propagated by 2₁-screw symmetry in each case. In acknowledgment of the distinct topologies, those with 2₁-screw symmetry are labelled as L. The differences between the polymorphs of [Hg(S₂P(O-i-Pr)₂)₂]ₙ primarily relate to differences in Hg–S bond lengths, with the range of Hg–S bond lengths in the C2/c polymorph of 2.39–2.89 Å [61] being greater than in the P2₁/c form of 2.44–2.83, corresponding to Δ(Hg–S) values of 0.50 and 0.39, respectively.

Figure 6. Aggregation in the crystals of (a) [Cd(S₂P(OMe)₂)₂]ₙ (25) and (b) [Cd(S₂P(O-s-Bu)₂)₂]ₙ (30).

Figure 7. Aggregation in the crystals of (a) [Hg(S₂P(OMe)₂)₂]ₙ (32) and (b) [Hg(S₂P(O-c-Pentyl)₂]ₙ (35).

3.3. Zinc-Triad Binary Dithiocarbamate Structures

By far the most numerous structures included in this review are the zinc-triad binary dithiocarbamates. While these generally adopt mononuclear or more likely binuclear motifs (see below), the presence of a heteroatom in the organic substituents can lead to further aggregation in the solid-state.

3.3.1. Zinc Dithiocarbamates

Data for the 65 Zn(S₂CNR')₂ structures discussed in this section, 36–100 [25,64–110], are collected in Table 3. The first motif noted is monomeric and designated M. The zinc atom in those structures adopting motif M is chelated by two dithiocarbamate ligands which are generally coordinating in...
a symmetric mode, for example, 2.32 and 2.35 Å in the structure of Zn(S$_2$CNCy)$_2$ (37) [25], illustrated in Figure 8a. This structure has the zinc centre located on a 2-fold symmetry axis; similar symmetry is also found in Zn(S$_2$CNMe)$_2$ (41) and Zn(S$_2$CPh)$_2$ (42) [65] and [71]. The coordination geometry is based on distorted tetrahedral S$_4$ environments as the ZnS$_2$C chelate planes are approximately orthogonal to each other. The assignment of monomeric structures is based on the lack of intermolecular Zn⋯S associations less than the sum of the van der Waals radii of zinc and sulphur, taken as 4.05 Å [20]. This is true for most of the examples, but in four structures, Zn⋯S less than the sum of the van der Waals radii is evident, that is, 42 (3.93 Å), 45 (3.86 Å), 39 (3.58 Å), and 43 (3.44 Å). Such alignment of molecules gives the potential for dimerization, leading to binuclear motifs N (39) and O (42, 43 and 45), as discussed below. Such a potential dimerization is illustrated in Figure 8b for 39.

Table 3. Summary of the general features of Zn(S$_2$CNRR')$_2$ structures 36–100.

| Compound | R/R' | Donor Set | Motif | Designation | Ref. |
|----------|------|-----------|-------|-------------|-----|
| 36       | CH$_2$CH$_2$OMe/CH$_2$CH$_2$OMe | S$_4$ | M | monomer | [64] |
| 37       | Cy/Cy | S$_4$ | M | monomer | [25] |
| 38       | Benzyl/Benzyl | S$_4$ | M | monomer | [66] |
| 39       | Me/Cy | S$_4$ | M | monomer | [67] |
| 40       | n-Pr/CH(Me)Et | S$_4$ | M | monomer | [68] |
| 41       | NR' = 3,4-dihydroquinoline | S$_4$ | M | monomer | [69] |
| 42       | n-Bu/5-t-Bu-3-Me-2-OH-benzyl | S$_4$ | M | monomer | [70] |
| 43       | CH$_2$CH$_2$OH/CH$_2$(ferrocenyl) | S$_4$ | M | monomer | [71] |
| 44       | (CH$_2$)$_3$OEt/3,5-di-t-Bu-4-OH-benzyl | S$_4$ | M | monomer | [72] |
| 45       | Benzyl/CH$_2$(1-Me-pyrrol-2-yl) | S$_4$ | M | monomer | [73] |
| 46       | Benzyl/4-OMe-benzyl | S$_4$ | M | monomer | [74] |
| 47       | Benzyl/R$^{1,1}$ | S$_4$ | M | monomer | [75] |
| 48       | CH$_2$(4-OMe-phenyl)/CH$_2$(2-furyl) | S$_4$ | M | monomer | [76] |
| 49       | Me/Me | S$_4$ | N | dimer | [77] |
| 50       | n-Bu/n-Bu | S$_4$ | N | dimer | [78] |
| 51       | n-Bu/n-Bu | S$_4$ | N | dimer | [79] |
| 52       | Me/CH$_2$(ferrocenyl) | S$_4$ | N | dimer | [80] |
| 53       | Et/Et | S$_4$ | O | dimer | [81] |
| 54       | n-Pr/n-Pr | S$_4$ | O | dimer | [82] |
| 55       | i-Pr/i-Pr | S$_4$ | O | dimer | [83] |
| 56       | CH$_2$(H)=CH$_2$/CH$_2$(H)=CH$_2$ | S$_4$ | O | dimer | [84] |
| 57       | CH$_2$CH$_2$OH/CH$_2$CH$_2$OH | S$_4$ | O | dimer | [85] |
| 58       | CH$_2$CH$_2$OH/CH$_2$CH$_2$OH | S$_4$ | O | dimer | [86] |
| 59       | CH$_2$CH$_2$OH/CH$_2$CH$_2$OH | S$_4$ | O | dimer | [87] |
| 60       | R + R' = (CH$_2$)$_3$ | S$_4$ | O | dimer | [88] |
| 61       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [89] |
| 62       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [90] |
| 63       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [91] |
| 64       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [92] |
| 65       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [93] |
| 66       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [94] |
| 67       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [95] |
| 68       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [96] |
| 69       | R + R' = (CH$_2$)$_5$ | S$_4$ | O | dimer | [97] |
| 70       | Me/Et | S$_4$ | O | dimer | [98] |
| 71       | Me/n-Pr | S$_4$ | O | dimer | [99] |
| 72       | Me/i-Pr | S$_4$ | O | dimer | [80] |
| 73       | Me/n-Bu | S$_4$ | O | dimer | [81] |
| 74       | Me/Ph | S$_4$ | O | dimer | [82] |
| 75       | Me/CH$_2$CH$_2$OH | S$_4$ | O | dimer | [83] |
| 76       | Me/CH$_2$CH$_2$OH | S$_4$ | O | dimer | [84] |
| 77       | Me/CH$_2$(OMe)$_2$ | S$_4$ | O | dimer | [85] |
| 78       | Me/CH$_2$(Het)(OMe)$_2$ | S$_4$ | O | dimer | [86] |
| 79       | Me/R$^{2,9}$ | S$_4$ | O | dimer | [87] |
| 80       | Et/i-Pr | S$_4$ | O | dimer | [88] |
The vast majority of the binary zinc dithiocarbamates are binuclear, adopting one of two motifs. The common feature of each motif is that there are equal numbers of chelating and bidentate bridging dithiocarbamate ligands, resulting in central, eight membered [SCSZn]2 rings. Transannular Zn⋯S interactions are noted within these rings. The differences between the motifs arise as a result of the relative disposition of the chelating ligands. In motif N, illustrated in Figure 8c for [Zn(S2CNMe2)2]2 (49) [76], both chelating rings are on the same side of the molecule, that is, the molecules have 2-fold or
close to 2-fold symmetry. In motif O, illustrated in Figure 8d for \([\text{Zn}(\text{S}_2\text{CN}(\text{Me})\text{Et})_2]_2\) \((53)\) [79], the chelating molecules lie on opposite sides of the central ring, that is, the molecules are disposed around a centre of inversion or are close to centrosymmetric. In terms of the central [-SCSZn] rings, in motif N, they adopt a boat form, whereas in motif O, they have the form of a chair. Of the 46 binuclear structures, four adopt motif N and 42 adopt motif O.

Motif N is adopted by four molecules, with 49, 50, and 52 each having crystallographically-imposed 2-fold symmetry, whereas 51 has pseudo 2-fold symmetry only. That there is a fine balance between the symmetry in the structures conforming to motif N is found in the polymorphs of \([\text{Zn}(\text{S}_2\text{CN}(\text{n-Bu})_2]_2\)

whereby 50 [77] is strictly symmetric and 51 [78] is not. The chelating dithiocarbamate ligands form very similar Zn-S bond lengths, with differences between them typically less than 0.1 Å, but those formed by the bidentate bridging ligands are even more symmetric. A common feature of each structure is the formation of transannular Zn···S interactions involving the bridging-sulphur atoms with separations normally in the range of 2.9–3.1 Å. Hence, the coordination geometry is described as \(S_4\) + 1. With \(\tau\) \([50]\) values between 0.39 (49) and 0.64 (51), the resultant coordination geometries are intermediate between the ideal square-pyramidal (\(\tau = 0.0\)) and trigonal-bipyramidal (\(\tau = 1.0\)).

The majority of the binary zinc(II) dithiocarbamates adopt the binuclear motif O, with the overwhelming majority of these molecules being disposed about a crystallographic centre of inversion. There is only one exception to this rule, whereby the binuclear molecule found in \([\text{Zn}(\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH})_2]_2\) \((76)\) [83] is disposed by a non-crystallographic inversion centre. This structure is a methanol solvate [83]. The same binuclear molecule is found in a di-hydrate (75) and is centrosymmetric [96]. The persistence of the centrosymmetric motif is also seen in the structures of \([\text{Zn}(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2]_2\) \((67)\) [92] and \([\text{Zn}(\text{S}_2\text{CN}(\text{Me})\text{Et})_2]_2\) \((70)\) [94] for each of which there are two crystallographically independent binuclear molecules, each disposed about a centre of inversion. The general trend in the observed Zn-S bond lengths for structures adopting motif N is also found for molecules adopting motif O, in that the bridging dithiocarbamate ligands form more symmetric Zn-S bonds than the chelating ligands. There are two sets of solvato-polymorphs amongst the compounds adopting motif O. The first, \([\text{Zn}(\text{S}_2\text{CN}(\text{Et})\text{Ph})_2]_2\)

is dimorphic, crystallising in monoclinic (\(P_2_1/c\)) and triclinic (\(P^\prime\)) space groups, that is, 83 [101] and 84 [102], respectively. The second set of polymorphs is found for trimorphic \([\text{Zn}(\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH})_2]_2\), which crystallises in orthorhombic (Pbcn; 57) [83], monoclinic (C2/c; 58) [84], and triclinic (\(P^\prime\)) [85] space groups. The molecules with motif N adopt \(S_4\) + 1 coordination geometries that are highly distorted. Using the values of \(\tau\) [50] as a measure, the coordination geometry most closely resembling an ideal square-pyramidal geometry (\(\tau = 0.0\)) is found in the triclinic polymorph of \([\text{Zn}(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2]_2\) \((59)\) [85], with \(\tau = 0.16\), and the one with a geometry resembling a trigonal-bipyramid (\(\tau = 1.0\)) is found in the structure of \([\text{Zn}(\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH})_2\text{CNEt}]_2\) \((79)\) [74], with \(\tau = 0.62\).

The adoption of motif mononuclear M as opposed to binuclear N and O can be partially explained in terms of the steric bulk of the nitrogen-bound substituents. For example, \([\text{Zn}(\text{S}_2\text{NC}_{\text{Cy}})_2]_2\) \((37)\) [25], with bulky cyclohexyl groups, is mononuclear, but when one cyclohexyl group is substituted by a smaller ethyl group to give \([\text{Zn}(\text{S}_2\text{CN}(\text{Et})\text{Cy})_2]_2\) \((82)\) [25], the binuclear O motif is formed. That other factors coming into play are evidenced by the structure of \([\text{Zn}(\text{S}_2\text{CN}(\text{Me})\text{Cy})_2]\) \((39)\) [66], where the ethyl group of 82 is replaced by a methyl group, as 39 adopts mononuclear motif, M. This fine balance is no better exemplified by the structure of \([\text{Zn}(\text{S}_2\text{CN}(\text{i-Bu})_2]_2\) \((95)\) [107], whereby two independent molecules comprise the crystallographic asymmetric unit, one mononuclear (motif M), and the other binuclear (motif O); neither molecule has crystallographic symmetry.

The five remaining structures to be described in this section carry potential nitrogen donor atoms in their nitrogen-bound substituents. In \([\text{Zn}(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{NMe})_2]_2\), \((96)\) [108], one of the nitrogen atoms of the 4-methylpiperazine residue coordinates a symmetry-related zinc atom to generate a one-dimensional coordination polymer with a zig-zag topology, as illustrated in Figure 9a. The resulting NS4 donor set is intermediate between the ideal square-pyramidal (\(\tau = 0.0\)) and trigonal-bipyramidal (\(\tau = 1.0\)) coordination geometries, as seen in the value of \(\tau = 0.56\) [50].
The structure of 96 is assigned motif P. Two structures, [ZnS₂CN(Benzy1)CH₂(3-py)]₂ₙ (97) [72], Figure 9b, and [ZnS₂CN(CH₂ferrocenyl)CH₂(3-py)]₂ₙ (98) [109], adopt motif Q, which is binuclear and located about a centre of inversion. Here, only one of the dithiocarbamate ligands employs the nitrogen atom in coordination with the second pyridyl-nitrogen atom being non-coordinating. In motif Q, the resulting aggregate is a dimer. The NS₄ donor set in 97 is close to a square-pyramid with \( \tau = 0.20 \) and the nitrogen atom occupying the apical position. With a value of \( \tau = 0.36 \), the coordination geometry in 98 is less regular than in 97. A coordination polymer with a zig-zag topology is found in the crystal of [ZnS₂CN(Et)CH₂(4-py)]₂ₙ 99 [110] as one of the dithiocarbamate ligands is bridging in a \( \mu₂\cdotκ³ \) coordination mode via two sulphur atoms and the pyridyl-nitrogen atom, Figure 9c; the other dithiocarbamate ligand for each of the two independent ZnS₂CN(Et)CH₂(4-py)₂ residues is chelating. The NS₄ coordination geometries are based on square-pyramidal geometries with \( \tau = 0.23 \) and 0.32 [110]. Despite having a pyridyl- rather than an amine-nitrogen donor, the structure of 99 is assigned to motif P as for 96.

![Figure 9](image-url)

**Figure 9.** (a) One-dimensional coordination polymer in [ZnS₂CN(CH₂CH₂)NMe₂]₂ₙ (96); (b) molecular structure of dimeric [ZnS₂CN(Benzy1)CH₂(3-py)]₂ₙ (97); and (c) one-dimensional coordination polymer in [ZnS₂CN(Et)CH₂(4-py)]₂ₙ (99).

The final binary zinc dithiocarbamate structure to be described, [ZnS₂CN(CH₂ferrocenyl)CH₂(4-py)]₂ₙ (100) [109], also carries pyridyl-nitrogen atoms in the organic substituents and in this case, both participate in coordination to symmetry-related zinc atoms. The resulting aggregation is
of a two-dimensional layer. As seen in the upper view of Figure 10, the layer is flat, with the ferrocenyl residues lying to either side. The N$_2$S$_4$ donor set in motif R is trans-octahedral.

### 3.3.2. Cadmium Dithiocarbamates

Several of the motifs adopted by the binary cadmium(II) dithiocarbamates, 101–141 [98,111–137], are closely related to those observed for their zinc counterparts. Over and above these, are several unprecedented polymeric structures. There is a complete lack of mononuclear, tetrahedral structures (motif M), reflecting the propensity of cadmium(II) to increase its coordination number. Data for the 41 known Cd(S$_2$CNRR$'$)$_2$ structures are collated in Table 4.

**Table 4. Summary of the general features of Cd(S$_2$CNRR$'$)$_2$ structures 101–141.**

| Compound | R/R' | Donor set | Motif | Designation | Ref. |
|----------|------|-----------|-------|-------------|------|
| 101      | n-Bu/n-Bu | S$_5$ | N | dimer | [111] |
| 102      | Et/Et | S$_5$ | O | dimer | [112,113] |
| 103      | n-Pr/n-Pr | S$_5$ | O | dimer | [114] |
| 104      | i-Pr/i-Pr | S$_5$ | O | dimer | [115] |
| 105      | CH$_2$C(H)=CH$_2$/CH$_2$C(H)=CH$_2$ | S$_5$ | O | dimer | [116] |
| 106      | i-Bu/i-Bu | S$_5$ | O | dimer | [117] |
| 107      | Cy/Cy | S$_5$ | O | dimer | [118] |
| 108      | Benzyl/Benzyl | S$_5$ | O | dimer | [119] |
| 109      | Benzyl/Benzyl | S$_5$ | O | dimer | [120] |
| 110      | CH$_2$C(H)=CH$_2$/CH$_2$C(H)=CH$_2$ | S$_5$ | O | dimer | [121] |
| 111      | R + R' = (CH$_2$)$_5$ | S$_5$ | O | dimer | [122] |
| 112      | R + R' = (CH$_2$)$_5$ | S$_5$ | O | dimer | [123] |
| 113      | R + R' = (CH$_2$)$_5$Me | S$_5$ | O | dimer | [124] |
| 114      | R + R' = (CH$_2$)$_5$ | S$_5$ | O | dimer | [125] |
| 115      | Me/Ph | S$_5$ | O | dimer | [126] |
| 116      | Et/Cy | S$_5$ | O | dimer | [118] |
| 117      | n-Pr/i-Pr | S$_5$ | O | dimer | [127] |
| 118      | i-Pr/CH$_2$C$_2$OH | S$_5$ | O | dimer | [128] |
| 119      | i-Pr/CH$_2$C$_2$OH | S$_5$ | O | dimer | [129] |
| 120      | i-Pr/CH$_2$C$_2$OH | S$_5$ | O | dimer | [129] |
| 121      | Benzyl/CH$_2$(2-furyl) | S$_5$ | O | dimer | [130] |
| 122      | Benzyl/CH$_2$C$_4$H$_4$3-Cl | S$_5$ | O | dimer | [131] |
| 123      | Benzyl/CH$_2$C$_4$H$_4$4-Cl | S$_5$ | O | dimer | [131] |
| 124      | Me/(CH$_2$)$_2$NMe$_2$ | NS$_4$ | Q | dimer | [132] |
| 125      | CH$_2$(3-py)/R$_1$ | NS$_4$ | Q | dimer | [133] |
| 126      | CH$_2$C$_2$H$_4$4-Cl/CH$_2$(furyl) | 2 x S$_5$ + S$_6$ | S | trimer | [131] |
| 127      | CH$_2$C$_2$H$_4$4-Cl/CH$_2$(furyl) | 2 x S$_5$ + S$_6$ | S | trimer | [133] |
| 128      | Me/(CH$_2$)$_2$NMe$_2$ | NS$_4$ | T | polymer | [134] |
| 129      | Et/CH$_2$(4-py) | N$_2$S$_4$ | U | double-layer | [135] |
| 130      | Benzyl/CH$_2$(3-py) | N$_2$S$_4$ | R | layer | [133] |
| 131      | CH$_2$(furyl)/CH$_2$(3-py) | N$_2$S$_4$ | R | layer | [133] |
| 132      | CH$_2$(thiophen-2-yl)/CH$_2$(3-py) | N$_2$S$_4$ | R | layer | [133] |
| 133      | CH$_2$(ferrocenyl)/CH$_2$(3-py) | N$_2$S$_4$ | R | layer | [109] |
| 134      | CH$_2$(3-py)/CH$_2$(3-py) | N$_2$S$_4$ | R | layer | [133] |
| 135      | Me/Me | S$_6$ | V | polymer | [136] |
| 136      | i-Pr/CH$_2$C$_2$OH | S$_6$ | V | polymer | [129] |
| 137      | Benzyl/R$_2$ | S$_6$ | V | polymer | [131] |
| 138      | CH$_2$(furyl)/CH$_2$C$_4$H$_4$4-F | S$_6$ | V | polymer | [131] |
| 139      | CH$_2$(furyl)/CH$_2$C$_4$H$_4$4-NO$_2$ | S$_6$ | V | polymer | [131] |
| 140      | Me/CH$_2$C(3-py)OMe | S$_6$ | W | polymer | [98] |
| 141      | i-Pr/CH$_2$C$_2$OH | S$_6$ | W | polymer | [128] |

1 di-dichloromethane solvate; 2 P$_2$/n polymorph; 3'R'1 polymorph; 4 monobenzene solvate; 5 di-ethanol solvate; 6 di-acetonitrile solvate di-hydrate; 7 1:2 co-crystal with 3-isopropyl-1,5-oxazolidine-2-thione; 8 R$_1$ is 1H-indol-3-ylmethyl; 9 3-methylpyridine solvate; 10 ethanol hemi-solvate; 11 R$_2$ is 1,3-benzoxioxol-5-CH$_2$; 12 1/3 acetonitrile solvate.
The coordination geometries tend to be closer to square-pyramidal for the molecules in this category. The transannular Cd-S interaction is considerably shorter at 2.89 Å than the equivalent interaction observed for the zinc analogues and therefore, the cadmium centre can be considered as five-coordinate. The S₅ donor set, with a value of τ = 0.50, is exactly intermediate between ideal square-pyramidal (τ = 0.0) and trigonal-pyramidal (τ = 1.0) geometries.

A considerably larger number of binuclear [Cd(S₂CNRR')₂]₂ structures, that is, 22, adopt the centrosymmetric analogue of motif N, that is, motif O, with archetypical [Cd(S₂CNEt₂)₂]₂ (102) [112,113] shown in Figure 11b. In most structures, the range of chelating and bridging Cd-S bond lengths is quite narrow, with the narrowest range of 2.58 to 2.59 Å being found in [Cd(S₂CN(CH₂)₅-4-Me)₂]₂ (113) [124]. There is only one exceptional structure where the Cd-S bond lengths span a considerably greater range, that is, in [Cd(S₂CN(i-Pr)CH₂CH₂OH)₂]₂ (120), isolated in a 1:2 co-crystal with 3-isopropyl-1,3-oxazolidine-2-thione [129], where the Cd-S bond lengths span a range of about 0.30 Å, that is, with bridging Cd-S bond lengths of 2.42 and 2.56 Å, and chelating bonds of 2.51 and 2.71 Å. The latter structure also presents the longest transannular contact of 3.05 Å. In the rest of the structures, these interactions are usually less than 2.85 Å, and as short as 2.74 Å, as in [Cd(S₂CN(i-Pr)CH₂CH₂OH)₂]₂ (119) [129], isolated as a di-acetonitrile solvate, di-hydrate. The coordination geometries tend to be closer to square-pyramidal for the molecules in this category. The most extreme coordination geometry is found in [Cd(S₂CN(Benzyl)CH₂(2-furyl))₂]₂ (121) [130] with τ = 0.0, with the bridging-sulphur atom occupying the apical position. Only three of the molecules have values of τ > 0.50, for example, [Cd(S₂CN(n-Pr)-i-Pr)₂]₂ (117) (τ = 0.51) and
\[ \text{[Cd[CN(n-Pr)CH}_2\text{C}_6\text{H}_4\text{-3-Cl}]}_2 \text{]_2 (122) [131]} \) \((\tau = 0.62)\). The third structure, \([\text{Cd[S}_2\text{CN(CH}_2)_3\text{Me}]_2]_2 \text{]_2 (111) [122]}\), has two independent molecules in the crystallographic asymmetric unit, with one of the molecules having \(\tau = 0.54\) and the other having \(\tau = 0.39\). The \([\text{Cd[S}_2\text{CN(Benzyl)}_2]_2]_2\) compound has been characterised in two polymorphs. In the triclinic form, \([108 [119]}\), \(\tau = 0.54\), and in the monoclinic form, \([109 [120]}\), with two independent molecules in the asymmetric unit, the values of \(\tau\) compute to 0.01 and 0.42.

The flexibility in the \([\text{Cd(S}_2\text{CNRR'}]}_2]_2\) molecules adopting motif \(O\) is clearly appreciated when one compares the pairs of structures \([108\text{ and 109 (coordination geometries), and 118 and 119 (Cd-S bond lengths).}\)

Two molecules, that is, \([\text{Cd[S}_2\text{CN(Me)}(\text{CH}_2)_3\text{NMe}_2]}_2]_2 \text{]_2 (124) [134]}\), Figure 11c, and \([\text{Cd[S}_2\text{CNCH}_2\text{(3-py)}(\text{1H-indol-3-ylmethyl)}]_2]_2 (125) [133]}\), adopt binuclear motif \(Q\) owing to the coordination of a nitrogen atom of an organic substituent to a symmetry related cadmium atom; both binuclear species are centrosymmetric. The five-coordinate indicator, \(\tau\), is 0.22 for 124 with the nitrogen atom in the apical position, and 0.42 for 125, indicating a more distorted geometry.

A new motif, trinuclear motif \(S\), is found in two structures, namely \([\text{Cd[S}_2\text{CN(CH}_2\text{C}_6\text{H}_4\text{-4-X)}\text{CH}_2(furyl)}]_2]_3\), for isostructural \(X = \text{Me} (126) [131]}\) and \(X = \text{Cl} (127) [133]}\), Figure 11d. The motif sees a central \(\text{Cd(dithiocarbamate)}_2\) residue associated with two other residues so that the cadmium atoms in the outer molecules have \(S_5\) coordination geometries, resembling the situation in motif \(O\). By contrast, the central cadmium atom is six-coordinate within a \(S_6\) donor set; each trinuclear molecule is located on a centre of inversion. In 126, the range of Cd-S bond lengths for the five-coordinate cadmium atom is 2.55 to 2.65 Å with the transannular distance being 2.71 Å, and the value of \(\tau\) is 0.30. The Cd-S bond lengths for the central cadmium span a wider range, that is, 2.59 to 2.89 Å. The equivalent parameters in 127 present very similar features and the same value for \(\tau\).

![Figure 11](image-url)

**Figure 11.** Molecular structures of (a) dimeric (2-fold symmetry) \([\text{Cd[S}_2\text{CN(n-Bu)}_2]_2]_2 (101)}\), (b) dimeric (inversion symmetry) \([\text{Cd[S}_2\text{CN(n-Bu)}_2]_2]_2 (102)}\), (c) dimeric \([\text{Cd[S}_2\text{CN(Me)}(\text{CH}_2)_3\text{NMe}_2]}_2]_2 (124)}\), and (d) trimeric \([\text{Cd[S}_2\text{CN(CH}_2\text{C}_6\text{H}_4\text{-4-Me)}\text{CH}_2(furyl)}]_2]_3 (127)}\).
channels in which solvent 3-methylpyridine molecules reside (not shown). The resultant N₂S₄ donor set is based on an octahedron and, crucially, the nitrogen donors occupy mutually cis-positions. In a clear difference, the remaining five structures with potential pyridyl-nitrogen atoms feature trans-N₂S₄ donor sets. This arrangement allows for the formation of two-dimensional arrays reminiscent of motif R, and an exemplar, Cd[S₂CN(Benzyl)CH₂(3-py)]₂n (130) [133], is illustrated in Figure 12c.

The distinctive feature in the seven crystals of 135–141 [98,128,129,131,136] is that each of the dithiocarbamate ligands adopts a μ₂κ³-coordination mode, leading to octahedral S₆ coordination geometries and one-dimensional chains. Five of the structures feature 2-fold symmetry with the cadmium atom located on the axis, whereas the chains are propagated by crystallographic inversion symmetry in the remaining two structures. Two views of the chain for [Cd(S₂CNMe)₂]ₙ (135) [136], being an exemplar for motif V, are shown in Figure 13a, and equivalent views for [Cd(S₂CN(i-Pr)CH₂)₂OH]₂n (141) [128], motif W, are shown in Figure 13b. The key difference between the chains, both of which have twisted topologies, is found in the orientation of the nitrogen-bound substituents, which are directed in the same direction in motif V, reflecting the

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**Figure 12.** Images of (a) one-dimensional [Cd[S₂CN(Me)]₂(CH₂)₂NMe₂]₂n (128); (b) the double-layer in [Cd[S₂CN(Et)]₂CH₂(3-py)]₂n (129); and (c) two-dimensional [Cd[S₂CN(Benzyl)]CH₂(3-py)]₂n (130).
2-fold symmetry, but in different directions for motif W, this time reflecting the inversion symmetry. The chains found in 136 [129] and 141 [128], that is, adopting motifs S and T, respectively, are supramolecular isomers [137], suggesting relatively small energy differences between the motifs. Further, solutions of each of 136 and 141 converted over time, within hours, into the dimeric motif O, that is, into 118 [128] and 119 [129], respectively, are consistent with the notion that the commonly observed binuclear motif is the thermodynamic outcome of the crystallisation of these compounds.

![Figure 13](image_url)

**Figure 13.** Side- and end-on views of one-dimensional chains in the crystals of (a) [Cd(S₂CNMe)₂]ₙ (135) and (b) [Cd[S₂CN(i-Pr)CH₂CH₂OH]₂]ₙ (141). Additional colour code: hydrogen, green.

### 3.3.3. Mercury Dithiocarbamates

Unlike the foregoing binary zinc(II) and cadmium(II) dithiocarbamates, the structural chemistry of the mercury(II) analogues features quite extensive supramolecular association based on secondary Hg⋯S interactions [138]. Key geometric data for the 44 Hg(S₂CNRR')₂ structures, 142–185 [39,70,101,105,139–163], described in this section are listed in Table 5. The exceptional series of structures, at least in terms of forming intermolecular Hg⋯S interactions, are strictly monomeric 142–145 [139–142], illustrated for Hg[S₂CN(i-Pr)₂]₂ (142) [139] in Figure 14a, as there are no intermolecular Hg⋯S contacts less than 4.0 Å in their respective crystals. Each of the four structures has the mercury atom lying as a 2-fold axis of symmetry and conforms to motif M, that is, distorted tetrahedral geometry within an S₄ donor set. In Hg(S₂CNCy)₂ (143) [140], the dithiocarbamate ligand chelates the mercury centre with symmetric Hg-S bond lengths of 2.53 and 2.54 Å, and the widest S-Hg-S angle is 142°. At the other extreme, for Hg(S₂CнBenzyl)₂ (144) [141], the dithiocarbamate ligand coordinates with asymmetric Hg-S bond lengths of 2.40 and 2.79 Å, and with the widest angle of 160° formed between the more tightly bound sulphur atoms.

Compounds 146–155 [39,70,101,105,143–147] also adopt motif M, but lack the symmetry exhibited by 142–145. The dithiocarbamate ligands generally coordinate with disparate Hg-S bond lengths, with the differences between the short and long bonds usually being 0.3–0.4 Å. Supramolecular molecular association between centrosymmetrically-related molecules is always found in 146–155, with intermolecular Hg⋯S separations ranging from a short 3.18 Å in Hg[S₂CN(CH₂CH₂OH)CH₂(ferrocenyl)]₂ (155) [70] to a long 3.85 Å in Hg[S₂CN(Benzyl)CH₂(1-Me-1H-pyrrol-2-yl)] (152) [146], much in the same way as discussed above for the transition of zinc dithiocarbamates between motifs M and O, see Figure 8. For mercury and sulphur, the sum of the van der Waals radii is assumed to be 3.35 Å [20]. An exemplar for the tendency towards dimerization in the mercury dithiocarbamates is shown in Figure 14b for Hg[S₂CN(CH₂)₄NCH₂C(H)=C(H)Ph] (147) [144].

Mononuclear motifs are also found for 156–160 [72,148–151], with the major difference being that the S₄ donor set is strictly square-planar, with the mercury atom located on a crystallographic centre of inversion in all cases except for Hg[S₂CN(CH₂CH₂OH)₂]₂ (160) [151]. Accordingly, this
series is assigned motif U. The dithiocarbamate ligands for motif U coordinate in an asymmetric mode, with the differences between long and short Hg-S bonds being around 0.6 Å; this contrasts with the symmetric square-planar geometries observed for motif D. The widest angle in the square-plane is 180° for all structures adopting motif X, including for non-symmetric Hg[S2CN(CH2CH2OH)2]2 (160) [151]. The alteration in geometry and increased asymmetry in the Hg-S bond lengths correlates with the formation of two intermolecular Hg···S interactions, leading to linear supramolecular chains in the respective crystals. The Hg···S separations range from 3.18 Å for one of the contacts in Hg[S2CN(CH2CH2OH)2]2 (160) [151] to 3.40 Å in Hg(S2CNMe)2 (156) [148]. This supramolecular association is shown in Figure 14c for Hg(S2CNEt2)2 (157) [150]. The extended coordination geometry is S4 + S2, with the weakly associated sulphur atoms mutually trans.

Table 5. Summary of the general features of Hg(S2CNRR′)2 structures 142–185.

| Compound | R/R’ | Donor Set | Motif | Designation | Ref. |
|----------|------|-----------|-------|-------------|------|
| 142      | i-Pr/i-Pr | S4 | M | monomer | [139] |
| 143      | Cy/Cy | S4 | M | monomer | [140] |
| 144      | Benzyl/Benzyl | S4 | M | monomer | [141] |
| 145      | R + R’ = (CH2)4 | S4 | M | monomer | [142] |
| 146      | i-Bu/i-Bu | S4 | K | monomer | [143] |
| 147      | R + R’ = (CH2)4NCH2C(H)≡C(H)Ph | S4 | M | monomer | [144] |
| 148      | N(RR’) = R’1 | S4 | M | monomer | [145] |
| 149      | Et/Ph | S4 | M | monomer | [101] |
| 150      | i-Pr/Cy | S4 | M | monomer | [143] |
| 151      | Me/Ph; n-Bu/Ph | S4 | M | monomer | [105] |
| 152      | Benzyl/CH2(1-Me-1H-pyrrol-2-yl) | S4 | M | monomer | [146] |
| 153      | Benzyl/CH2(ferrocenyl) | S4 | M | monomer | [147] |
| 154      | CH2(3-py)/CH2(1-Me-1H-pyrrol-2-yl) | S4 | M | monomer | [39] |
| 155      | CH2CH2OH/CH2(ferrocenyl) | S4 | M | monomer | [70] |
| 156      | Me/Me | S4 | X | monomer | [148] |
| 157      | Et/Et | S4 | X | monomer | [149] |
| 158      | Benzyl/CH2(3-py) | S4 | X | monomer | [72] |
| 159      | Benzyl/CH2(4-py) | S4 | X | monomer | [150] |
| 160      | CH2CH2OH/CH2CH2OH | S4 | X | monomer | [151] |
| 161      | n-Bu/CH2(1H-pyrrol-2-yl) | S4 | Y | monomer | [152] |
| 162      | CH2(4-py)/CH2(1H-pyrrol-2-yl) | S4 | Z | monomer | [146] |
| 163      | Et/Et | S4 + 1 | O | dimer | [149,153] |
| 164      | i-Pr/i-Pr | S4 + 1 | O | dimer | [154] |
| 165      | n-Bu/n-Bu | S4 + 1 | N | dimer | [143] |
| 166      | R + R’ = (CH2)4 | S4 + 1 | O | dimer | [155] |
| 167      | R + R’ = (CH2)6Me | S4 + 1 | O | dimer | [156] |
| 168      | R + R’ = (CH2)6 | S4 + 1 | O | dimer | [157] |
| 169      | CH2(2-furyl)/CH2(2-furyl) | S4 + 1 | O | dimer | [158] |
| 170      | Me/Ph | S4 + 1 | O | dimer | [159] |
| 171      | Me/(CH2)2Ph | S4 + 1 | O | dimer | [160] |
| 172      | Et/Cy | S4 + 1 | O | dimer | [143] |
| 173      | Et/Ph | S4 + 1 | O | dimer | [161] |
| 174      | i-Pr/CH2CH2OH | S4 + 1 | O | dimer | [162] |
| 175      | Benzyl/CH2(2-furyl) | S4 + 1 | O | dimer | [158] |
| 176      | (CH2)2Ph/CH2(2-furyl) | S4 + 1 | O | dimer | [163] |
| 177      | (CH2)2Ph/CH2CH2(thiophen-2-yl) | S4 + 1 | O | dimer | [163] |
| 178      | CH2(3-py)/CH2(ferrocenyl) | S4 + 1 | O | dimer | [109] |
| 179      | CH2(3-py)/CH2(1-naphthyl) | NS4 | Q | dimer | [39] |
| 180      | NRR’ = R’2.5 | 2 × S4 + S8 | S | trimer | [145] |
| 181      | Me/CH2(4-py) | NS4 | Z | polymer | [72] |
| 182      | CH2(3-py)/CH2(1,3-benzodioxo-5-yl) | NS4 | P | polymer | [72] |
| 183      | CH2(4-py)/CH2(2-furyl) | N2S4 | R | layer | [72] |
| 184      | (CH2)2Ph/CH2(3-py) | NS5 | AA | polymer | [72] |
| 185      | (CH2)2Ph/CH2(1H-pyrrl-2-yl) | S8 | V | polymer | [152] |

1 R1 is 3,4-dihydroquinoline-1(2H); 2 tolyl hemi-solvate; 3 mono-ethanol solvate; 4 mono-pyridine solvate; 5 R2 is 1,2,3,4-tetrahydroquinoline.
Supramolecular aggregation via intermolecular Hg···S secondary bonding interactions is also found in each of Hg[S2CN(n-Bu)CH2(1H-pyrrol-2-yl)] (161) [152] and Hg[S2CN(CH2(4-py))CH2(1H-pyrrol-2-yl)] (162) [146]. In 161, relatively small differences in the Hg-S bond lengths, that is, 2.48 to 2.65 Å, are noted in the distorted tetrahedral geometry, with the widest angle being 138°. The sulphur atoms forming the shorter Hg-S bonds form bridging interactions (Hg···S = 3.48 and 3.61 Å) to symmetry-related molecules to sustain a weakly associated chain with a twisted topology, Figure 14d. The molecule in 162 has the mercury atom located on a 2-fold axis of symmetry, with the dithiocarbamate chelating with similar Hg-S bond lengths of 2.50 and 2.64 Å and the widest angle being 142°. Molecules also self-associate via very weak Hg···S interactions of 3.82 Å to form a twisted one-dimensional aggregation pattern, as shown in Figure 14e. Each of the independent supramolecular synthons in 161 is symmetric, four-membered [⋯S-Hg][2], and with a rectangular appearance. By contrast, in 162, the synthon is non-symmetric [⋯S-Hg-S···Hg] and has the appearance of a distorted diamond. With these differences, the structures found in 161 and 162 are assigned as motifs Y and Z, respectively.

The familiar binuclear motif seen in the zinc and cadmium dithiocarbamates is adopted by 16 mercury dithiocarbamate structures, 163–178 [109,143,149,153–163]. Being 2-fold symmetric, [Hg(S2CN(n-Bu)2]2 (165) [143] is assigned motif N, with the rest of the molecules being motif O. With two exceptions, the molecules adopting motif O are centrosymmetric; in [Hg(S2CN(Benzyl) CH2(2-furyl))]2 (175) [158], two independent centrosymmetric molecules comprise the asymmetric unit, and in [Hg(S2CN(Me)CH2Ph)]2 (171) [160], the molecule crystallises across a non-crystallographic...
centre. The mercury containing structures resemble the zinc analogues more than the cadmium structures, as the transannular Hg⋯S interaction is generally long, at least when compared to the sum of the van der Waals radii of 3.35 Å [20]. Hence, the coordination geometry is best described as being based on an S_4 + 1 arrangement. The values calculated for τ [50] indicate geometries tending towards square-pyramidal (τ = 0.0), with the minimum value of 0.01 being found for {Hg[S_2CN(i-Pr)CH_2CH_2OH]_2} [174] [162], and with all other structures, but one, having τ < 0.32. The exceptional structure, [Hg[S_2CN(CH_2(3-py))CH_2(2-ferrocenyl)]_2] [178] [109], has a τ value of 0.52. {Hg[S_2CN(n-Bu)_2]_2} [165] [143], having motif L, had a value of τ = 0.48. There are non-systematic variations in the Hg-S bond lengths although the range of the Hg-S bond lengths is relatively narrow, as exemplified by the aforementioned [Hg[S_2CN(Benzyl)CH_2(2-furyl)]_2] [175] [158] structure, with two independent molecules, where the range of Hg-S bond lengths of 2.46 to 2.73 Å encompasses most of the Hg-S separations in the other structures, with two exceptions. Before discussing these, it is relevant to note the range of transannular interactions within the eight-membered {-HgSCS} motif [163], Figure 14c, and binuclear {Hg(S_2CN)CH_2OH}_2 [174] [162], whereby the transannular interactions are shorter than the bridging Hg-S bond to the symmetry-related mercury atom. Under these circumstances, these structures represent a transition from motif M to motif O, but are assigned to the latter as all Hg-S separations are less than the sum of the respective van der Waals radii.

The capricious behaviour relating to coordination geometries, Hg-S bond lengths, and supramolecular association via Hg⋯S secondary bonding interactions is no better illustrated than for the pair of structures, mononuclear and square-planar Hg(S_2CNEt)_2 [157] [149], which self-associates into a supramolecular chain via Hg⋯S contacts, Figure 14c, and binuclear [Hg(S_2CNEt)_2]_2 [163] [149,153], Figure 15a; that is, the same compound can adopt either motif X or O, respectively. Similarly, strictly mononuclear Hg[S_2CN(i-Pr)]_2 [142] [149], motif M, in one polymorph can also adopt binuclear motif O in another, as in 164 [154].

![Figure 15](image-url)  
Figure 15. Molecular structures of (a) binuclear [Hg(S_2CNEt)_2]_2 (163); (b) binuclear [Hg(S_2CN[CH_2(3-py))CH_2(1-naphthyl)]_2] (179); and (c) trinuclear [Hg(S_2CNR^2)_2]_3 (180), where NR^2 is 1,2,3,4-tetrahydroquinoline. The dashed Hg⋯S bonds represent weak interactions.
The two remaining zero-dimensional aggregates among the binary mercury dithiocarbamates have precedents in their lower congeners. The centrosymmetric binuclear compound, \([\text{Hg}[\text{S}_2\text{CN}\text{CH}_2(3\text{-py})]\text{CH}_2(1\text{-naphthyl})]_2\) \((179)\) \([39]\), Figure 15b, has one chelating dithiocarbamate ligand and one bridging ligand, whereby one end chelates a mercury atom and bridges another via the pyridyl-nitrogen atom; this structure conforms to motif Q. The NS4 coordination geometry is almost intermediate between the ideal square-pyramidal \((\tau = 0.0)\) and trigonal-bipyramidal \((\tau = 1.0)\) as the value of \(\tau\) is calculated to be 0.48. The molecule of \([\text{Hg}[\text{S}_2\text{CNR}^2]_2]_3\) \((180)\) \([145]\) is trinuclear, Figure 15c, and allowing for differences in M-S separations, closely resembles motif S; NR2 is 1,2,3,4-tetrahydroquinoline. The central mercury atom in 180 is located on a centre of inversion, is coordinated asymmetrically \((2.37\) and \(2.95\) \(\text{Å}\)) by two dithiocarbamate ligands, and is connected to the two outer \(\text{Hg}[\text{S}_2\text{CNR}]_2\) residues by \(\text{Hg}\cdots\text{S}\) contacts of \(3.05\) and \(3.37\) \(\text{Å}\), that is, within and just outside the sum of the van der Waals radii value of \(3.35\) \(\text{Å}\) \([20]\). Thus, the coordination geometry for the central mercury atom resembles that seen in motif X, which is best described as \(\text{S}_4 + \text{S}_2\) with the weakly bound sulphur atoms in trans positions. The outer mercury atoms adopt heavily distorted five-coordinate geometries, as seen in the value of \(\tau = 0.33\), resembling the geometries found for the majority of structures adopting motif O.

There are five binary mercury dithiocarbamate structures that adopt one- or two-dimensional aggregation patterns in their crystals. The first of these, \([\text{Hg}[\text{S}_2\text{CN}(\text{Me})\text{CH}_2(4\text{-py})]_2]_n\) \((181)\) \([72]\), features an S,S-chelating dithiocarbamate ligand and another which chelates the same mercury atom while at the same time bridging a symmetry-related ligand to form a linear one-dimensional polymer, Figure 16a. The resulting NS4 donor set is based on a square-pyramidal geometry, with the calculated value of \(\tau\) being \(0.07\) compared to the ideal value for a square-pyramid of \(\tau = 0.0\) \([50]\). In this description, the nitrogen atom occupies an apical position. This linear aggregation does not have a precedent herein, so is assigned motif Z. In \([\text{Hg}[\text{S}_2\text{CN}(\text{CH}_3(2\text{-py}))\text{CH}_2(1,3\text{-benzodioxo-5-yl})]_2]_n\) \((182)\) \([72]\), which has only one pyridyl-nitrogen donor atom per repeat unit, compared with two in 181, a different aggregation pattern is found, Figure 16b. The modes of coordination of the dithiocarbamate ligands in 182 are as for 181 but, in the former, these generate zig-zag chains being propagated by glide-symmetry. The NS4 donor set is also as for 181 but, the distortion is greater from the ideal geometry, with \(\tau\) being \(0.20\). This coordination polymer, with precedents, is assigned as motif P.

![Figure 16](image-url)  
Figure 16. One-dimensional aggregation in (a) \([\text{Hg}[\text{S}_2\text{CN}(\text{Me})\text{CH}_2(4\text{-py})]_2]_n\) \((181)\) and (b) \([\text{Hg}[\text{S}_2\text{CN}[\text{CH}_2(4\text{-py})]\text{CH}_2(1,3\text{-benzodioxo-5-yl})]_2]_n\) \((182)\).
In [Hg[S₂CN(CH₂(4-py))]CH₂(2-furyl)]₂ₙ (183) [72], both pyridyl-nitrogen atoms are involved in the coordination to mercury, Figure 17, in contrast to the situation in each of 181 and 182. The extra participation of the pyridyl-nitrogen atoms results in a trans-N coordination to mercury, Figure 17, in contrast to the situation in each of 181 and 182. The coordination geometries for each is very similar, with the independent bridging Hg–S distances being 2.90 and 2.92 Å. The relationship to motif O is apparent in that each repeat unit participates in one accepting and one donating Hg–S interaction, but in motif AA, these occur on either side of the molecule to generate a chain rather than a dimer, as in O. The values of τ for each of the independent mercury atoms are equal at 0.57, consistent with highly distorted S₃ coordination geometries. The last structure to be described, that is, [Hg[S₂CN(CH₂)₂Ph]CH₂(1H-pyrrolyl-2-yl)]₂ₙ (185) [152], conforms to motif V, being a linear coordination polymer, Figure 18b, as each dithiocarbamate ligand is tri-connective, chelating one mercury atom while simultaneously bridging another; the mercury atom lies on a 2-fold axis.

A distinct motif, motif AA, is found in the crystal of [Hg[S₂CN(CH₂)₂Ph]CH₂(3-py)]₂ₙ (184) [72]. There are two independent Hg[S₂CN(CH₂)₂Ph]CH₂(3-py) units in the asymmetric unit and these are connected into a supramolecular polymer. As viewed from Figure 18a, the coordination geometry for each is very similar, with the independent bridging Hg–S distances being 2.90 and 2.92 Å. The coordination to mercury, Figure 18, in contrast to the situation in each of 181 and 182. The extra participation of the pyridyl-nitrogen atoms results in a trans-N coordination polymer, Figure 18b, as each dithiocarbamate ligand is tri-connective, chelating one mercury atom while simultaneously bridging another; the mercury atom lies on a 2-fold axis.

**Figure 17.** Two-dimensional aggregation in [Hg[S₂CN(CH₂(4-py))]CH₂(2-furyl)]₂ₙ (183).

**Figure 18.** One-dimensional aggregation in (a) [Hg[S₂CN(CH₂)₂Ph]CH₂(3-py)]₂ₙ (184) and (b) [Hg[S₂CN(CH₂)₂Ph]CH₂(1H-pyrrolyl-2-yl)]₂ₙ (185).

**4. Overview and Conclusions**

The foregoing bibliographic overview highlights the diverse structural chemistry exhibited by the binary zinc-triad 1,1-dithiolates, with 27 distinct structural motifs documented. The observed diversity
in their crystals is correlated, in part, with the different bonding requirements of the zinc, cadmium, and mercury centres. The nature of the 1,1-dithiolate ligand also plays a determining role, with bridging propensities being the greatest for xanthate and dithiophosphate ligands. Dithiocarbamates, by virtue of the significant contribution (40%) of the $^{2-}S_2C=N^+RR'$ anion to the overall electronic structure, are very effective chelators for metal centres and tend to be less likely to be engaged in extensive bridging interactions. In the context of the design of extended networks, this shortcoming can be overcome by incorporating other potential donor atoms in the organic substituents in the ligands, most notably pyridyl-nitrogen donors, to promote supramolecular aggregation. Steric effects exerted by the organic substituents can influence the supramolecular aggregation, in particular by militating weaker M-S bonds/M···S secondary bonding interactions. The above notwithstanding, very significant differences are evident among the 27 identified structural motifs, that is, between closely related compounds or even between polymorphs, and the challenge remains to rationalise the appearance of these and ultimately to use this information to predict structures based on chemical composition.

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