Steric control over C=O...C=O interactions in M(S₂COR)₂(dafone) compounds: M = Zn and Cd; R = Me, Et and iPr; dafone = 4,5-diazafluoren-9-one-N,N’

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Abstract. Crystallography shows that with the smaller xanthate-bound methyl groups in Zn(S₂COMe)₂(dafone) (1) and Cd(S₂COMe)₂(dafone) (3) anti-parallel C=O...C=O interactions link molecules into dimers. These are further associated via π−π interactions into a supramolecular chain, and in the case of 3 into a supramolecular two-dimensional array via C−H...S contacts. Increasing the size of the organic residue, i.e., to ethyl and isopropyl in Zn(S₂COEt)₂(dafone) (2), Cd(S₂COEt)₂(dafone) (4) and Cd(S₂CO-iPr)₂(dafone) (5), does not allow for the formation of this supramolecular architecture. Instead, supramolecular chains are sustained by C−H...S and C−H...π(chelate) interactions (the latter exclusively in the case of 5). The presence of recognisable/significant π−π and C−H...S and C−H...π(chelate) interactions is not consistent amongst the series yet only two crystal packing patterns are noted depending on the presence of the C=O...C=O interactions. This observation points to the importance of overall crystal packing considerations of bimolecular species in 1 and 3, and mononuclear species in 2, 4 and 5.

1. Introduction

Unlike their carboxylate counterparts, which are ubiquitous in forming coordination polymers including metal-organic framework structures (for discussions on terminology see [1, 2]), crystal engineering studies on 1,1-dithiolates such as dithiocarbamates (S₂CNR₂) [3, 4], xanthates (S₂COR) [5] and dithiophosphates (S₂P(OR)₂) [6, 7] are less advanced. While dithiocarbamates continue to attract great interest, one reason for their lack of application in the construction of coordination polymers relates to their propensity to chelate rather than bridge metal centres owing to the significant contribution to the overall electronic structure of the C²−S₂C=N⁺R₂ canonical form. This notwithstanding, owing to their comparative ease of synthesis, their ready derivatisation, stability and propensity to form crystals, crystal engineering lessons have been learnt from systematic studies of closely related 1,1-dithiolate structures, a pillar of crystal engineering [8].

A key finding arising from methodical analyses of metal 1,1-dithiolates is the observation that derivatives with larger organic substituents, either resident on the ligand or even on the metal centre, are less likely to form supramolecular M...S secondary bonds [9, 10] than those derivatives with smaller organic substituents, as larger substituents preclude close approach of the molecules [11–15]. Gratifyingly, this principle can be applied to rational construction of coordination polymers in their polyfunctional pyridyl adducts [16–21]. One method of overcoming the reluctance of dithiocarbamate ligands to bridge metal centres is to functionalise these to carry residues capable of hydrogen bonding, a strategy that has enabled the construction of various supramolecular architectures [22–26]. These approaches, i.e, increasing steric bulk of remote substituents, complexing with bridging pyridyl ligands or even functionalising the 1,1-dithiolate ligands, disrupt the ability of the individual molecules to associate via M...S secondary bonding. This principle is in fact well known having been observed previously in adducts with chelating ligands such as 2,2’-bipyridine and 1,10-phenanthroline: in these structures, non-classical C−H...M(chelate) interactions are often found [5, 27]. Exploiting the principles of metalloaromaticity [28, 29], C−H...M(chelate) interactions were first described for metal 1,1-dithiolates in the structures of Cd(S₂COR)₂(2,2’-bipyridine), R = nBu and CH₂CH₂OMe [30], and complement similar C−H...M(chelate) interactions found in systematic studies of acetylacetone complexes [31] and other chelating ligands, including porphyrins [32–37]. As a continuation of these studies and in keeping with the notion that C−H...M(chelate) interactions are by their very nature weak, it was thought of interest to functionalise the chelat-
Synthons are still lacking [52–56]. Generally, crystal engineering studies of these C–O interactions in organic crystal structures was established well over a decade ago [38], complimenting their ability to stabilise α-helices [43] and β-strands [44] in macromolecular systems with interest continuing today in their role in stabilising amide carbonyl…carbonyl interactions [45, 46]. There are three motifs characterising C–O…C–O interactions [38], namely (a) anti-parallel, (b) perpendicular and (c) sheared parallel, as illustrated in Fig. 1. In the original survey of all-organic molecules, the anti-parallel mode of association between carbonyl residues was shown more likely to be formed than in organic ketones, demonstrating that not only were such C–O…C–O interactions more likely to be formed than in organic ketones, the perpendicular motif was more prevalent [47]. A clear relationship between carbonyl residues was shown in organic crystal structures was established well over a decade ago [38], namely (a) anti-parallel, (b) perpendicular and (c) sheared parallel, as illustrated in Fig. 1. In the original survey of all-organic molecules, the anti-parallel mode of association between carbonyl residues was shown to dominate [38]. By contrast, in a subsequent survey of transition metal carbonyl, TM–C=O, structures it was demonstrated that not only were such C–O…C–O interactions more likely to be formed than in organic ketones, the perpendicular motif was more prevalent [47]. A clear influence of steric hindrance upon these interactions was also evident [47]. Despite comments on the prevalence of C–O…C–O interactions in “one-off” structural papers [48–51], generally crystal engineering studies of these synths are still lacking [52–56].

Herein, the crystal and molecular structures of a series of 1:1 adducts of M(S2COR)2 [M = Zn and Cd; R = Me, Et and iPr] with 4,5-diazafurozen-9-one-N,N′ (dafone) are described, Fig. 2, and an evaluation of the persistence of C=O…C=O interactions in these structures discussed.

2. Experimental

2.1 Characterisation

Infrared data were recorded as KBr discs on a FT-IR JASCO 650 spectrophotometer, and 1H NMR spectra were recorded on Bruker Avance 300 spectrometer. The 1H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using the chemical shifts of residual protio solvent resonance (CDCl3, δ 7.26).

2.2 Synthesis

The (HS2COR)2 [M = Zn, Cd, R = Me, Et and iPr] starting materials were prepared in high yields from the reaction of M(NO3)2 · nH2O (M = Zn, n = 6; M = Cd n = 4) and the respective potassium O-alkyl dithiocarbonate in aqueous solution. The dafone adducts were obtained from stirring at room temperature the parent M(S2COR)2 (0.2 g) with one stoichiometric amount of dafone (4,5-diazafurozen-9-one-N,N′), prepared following the literature procedure [57], in ethanol for each of 1–5. The solvent was removed in vacuo and crystals were grown as indicated below.

Zn(S2COMe)2(dafone) (1). Crystals were isolated from the slow evaporation of its ethanol solution. IR (cm−1): 1732 ν(C=O), 1200, 1146 ν(C–O), 1047 ν(C–S).

1H NMR: δ 6.49 (s, 6 H, CH3), 7.49 (dd, 2 H, CH, J = 7.5 & 5.0 Hz), 8.11 (d, 2 H, J = 7.5 Hz), 8.87 (d, 2 H, CH, J = 5.0 Hz). M. Pt > 450 °C.

Zn(S2COEt)2(dafone) (2). Crystals were isolated from the slow evaporation of its ethanol/pentane solution. IR (cm−1): 1732 ν(C=O), 1203, 1120 ν(C–O), 1043 ν(C–S).

1H NMR: δ 1.38 (t, 6 H, CH3, J = 7.0 Hz), 4.43 (q, 4 H, CH2, J = 7.0 Hz), 7.62 (dd, 2 H, CH, J = 7.5 & 5.0 Hz), 8.03 (d, 2 H, CH, J = 7.5 Hz), 8.83 (d, 2 H, CH, J = 5.0 Hz). M. Pt: 142–143 °C.

Cd(S2COMe)2(dafone) (3). Crystals were isolated from the slow evaporation of its tetrahydrofuran solution. IR (cm−1): 1732 ν(C=O), 1198, 1147 ν(C–O), 1047 ν(C–S).

1H NMR: δ 4.06 (s, 6 H, CH3), 7.53 (dd, 2 H, CH, J = 7.5 & 5.0 Hz), 8.12 (d, 2 H, J = 7.5 Hz), 8.89 (d, 2 H, CH, J = 5.0 Hz). M. Pt: > 450 °C.

Cd(S2COEt)2(dafone) (4). Crystals were isolated from slow evaporation of its methanol/dichloromethane solution. IR (cm−1): 1732 ν(C=O), 1201, 1120 ν(C–O), 1033 ν(C–S).

1H NMR: δ 1.43 (t, 6 H, CH3, J = 7.0 Hz), 4.44 (q, 4 H, CH2, J = 7.0 Hz), 7.62 (dd, 2 H, CH, J = 7.5 & 5.0 Hz), 8.15 (d, 2 H, CH, J = 7.5 Hz), 8.95 (d, 2 H, CH, J = 5.0 Hz). M. Pt: 155 °C.
2.3 Crystal structure determination

Intensity data for 1 were measured at 293 K on a Bruker AXS SMART CCD diffractometer fitted with MoKα radiation. Data processing and absorption corrections were accomplished with SMART and SAINT [59], respectively. Intensity data for 2–5 were measured at reduced temperatures on a Rigaku AFC12/Saturn724 CCD fitted with MoKα radiation. Data processing and absorption correction were accomplished with Crystal Clear [60] and ABSCOR [61], respectively. Details of cell data, X-ray data collection, and structure refinement are given in Table 1.

The structures were solved by direct methods [62]. Full-matrix least-squares refinement on F2 with anisotropic displacement parameters for all non-hydrogen atoms was performed [62]. The C-bound H atoms were placed on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.2 times (1.5 times for methyl-H) the value of the equivalent isotropic displacement parameter of the respective carrier atom. A weighting scheme of the form w = 1/[o2(Fo2)2 + (ap)2 + bp] where P = (Fo2 + 2Fe2)2/3 was introduced in each case. The maximum and minimum residual electron density peaks after the final refinement of 4 of 0.69 and −1.06 e Å−3, respectively, were located 0.75 Å and 0.81 Å from the Cd atom. In 2, atom C6 had high thermal motion but multiple sites were not resolved. By contrast, in 4, the equivalent atom was modelled over two sites and from anisotropic refinement, the major component has a site occupancy factor of 0.76(3). The programs WinGX [63], PLATON [64], ORTEP-3 for Windows [65] at the 35 (4 and 5), 50 (1 and 2) and 70% (3) probability levels and DIAMOND [66] were also used in the study.

### 3. Results

#### 3.1 Molecular structures

Two distinct but closely related coordination geometries are observed for 1–5, Fig. 2; salient geometric parameters

#### Table 1. Crystallographic data and refinement details for 1–5

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<th>Compound</th>
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<th>3</th>
<th>4</th>
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<td>C15H2CdN2O4S4</td>
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<td>P21/c</td>
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<td>35.040(3)</td>
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<td>36.079(3)</td>
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<td>0.028; 0.028</td>
<td>0.061; 0.069</td>
<td>0.061; 0.062</td>
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<td>0.027; 1.091</td>
<td>0.040; 39.331</td>
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<td>0.078; 0.079</td>
<td>0.064; 0.065</td>
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<td>0.127; 0.127</td>
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1: Supplementary Material: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-882728 and 882732. Copies of available material can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-363063 or e-mail: deposit@ccdc.cam.ac.uk). The list of F,F,F-data is available from the author up to one year after the publication has appeared.
are collected in Table 2. In the molecular structure of Zn(S₂COMe)_2 (dafone) (1), Fig. 3a, the zinc atom is coordinated by two asymmetrically chelating xanthate ligands with Δ(Zn–S) = difference in bond lengths) values of 0.33 and 0.26 Å, as well as a chelating dafone ligand which forms experimentally distinct Zn–N bond lengths [Δ(Zn–N) = 0.05 Å]. The resulting N₂S₄ donor set is approximately octahedral with distortions traced to the restricted bite angles of the chelating ligands. In this arrangement, each of the dafone-nitrogen atoms is approximately \( \text{trans} \) to a more weakly coordinating sulphur atom, Table 2. While the basic coordination geometry in Zn(S₂COEt)_2 (dafone) (2), Fig. 3b, is as just described, differences occurs in that i) there is a marked symmetrisation in the coordination modes of the chelating ligands \( \Delta(Zn–S) = 0.08 \) and \( 0.02 \text{ Å} \) and \( \Delta(Zn–N) = 0.01 \text{ Å} \), achieved by the lengthening of the shorter and shortening of the longer bonds of each chelate, and ii) one of the nitrogen atoms (N2) is now \( \text{trans} \) to a more strongly coordinating sulphur atom (S1).

The Cd(S₂COMe)_2 (dafone) (3) compound, Fig. 4a, is isostructural with 1, and each of Cd(S₂COEt)_2 (dafone) (4), Fig. 4b, and Cd(S₂CO-iPr)_2 (dafone) (5), Fig. 4c, is isostructural with 2. In 3, the chelating ligands coordinate more symmetrically than in 1 \( \Delta(Cd–S) = 0.25 \) and 0.05 Å and \( \Delta(Cd–N) = 0.04 \text{ Å} \) but less symmetrically than in 4 \( \Delta(Cd–S) = 0.07 \) and 0.02 Å and \( \Delta(Cd–N) = 0.01 \text{ Å} \) and 5 \( \Delta(Cd–S) = 0.08 \) and 0.05 Å and \( \Delta(Cd–N) = 0.02 \text{ Å} \). The general reduction in asymmetry in the mode of coordination of the chelating ligands in the cadmium structures is correlated with the longer distances and concomitant reduced steric pressure about the central cadmium atoms in 3–5 compared with 1 and 2. Other systematic variations are discussed below as these are correlated with the supramolecular aggregation patterns.

### 3.2 Supramolecular structures

The key feature of the crystal packing of 1 is the formation of C–O…C–O interactions between centrosymmetrically related carboxyl groups implying an ideal anti-parallel arrangement. The C15…O3' distance is 2.998(5) Å and the O3=C15…O3' angle is 94.9(3)° (symmetry op-
Based on standard distance criteria [64] (see discussion below) no other significant intermolecular interactions are noted in the crystal structure of 1; a view of the global crystal packing is given in Fig. 5b. A distinct supramolecular aggregation pattern is observed in the crystal structure of 2 which differs from 1 by having an O-bound ethyl group as opposed to an O-bound methyl group.

The first obvious difference in the crystal packing of 2 is the absence of C=O⋯C=O interactions. This is explained in terms of steric hindrance; calculations show that the electronic structures of xanthate anions are not influenced significantly by the organic substituent [67]. Referring to Fig. 5a, two of the methyl-H atoms form close intra-chain interactions [the H⋯S and H⋯O distances = 3.04 and 2.76 Å, respectively] even if beyond the standard criterion for “significant” intermolecular interactions [64], indicating a compact arrangement. If the supramolecular chain observed in 1 was maintained in 2, there would be impossible steric clashes owing to the greater size of ethyl compared with methyl. Accordingly, the supramolecular chain is not formed. While this does not inherently preclude the formation of C=O⋯C=O interactions in 2, whereby the dimeric units are assembled via other intermolecular interactions, a stable three-dimensional arrangement is formed in their absence, as described below.

Supramolecular chains are found in 2, see Figs. 6a and 6b, being mediated by C3–H⋯S2 interactions, involving both aromatic- and methyl-H atoms, as well as C15–H⋯π(chelate ring = ZnS3S4C4) interactions, Table 3. The aromatic-C15–H atom is bifurcated forming both C15–H⋯S3 and C–H⋯π(ZnS3S4C4) interactions to link translationally related molecules into a linear chain along the c-axis (see further Discussion below). Through the application of 1 symmetry, three such chains are linked into a helical assembly. The helical chains are connected into a three-dimensional architecture by π–π interactions between pyridyl rings, Table 3 and Fig. 6c.

As mentioned above, the zinc and cadmium structures, 1 and 3, are isostructural and each feature C=O⋯C=O interactions. In 3, the C15⋯O3’ distance is 3.017(2) Å and the O3⋯C15⋯O3’ angle is 96.21(16)° (symmetry operation i: 1 − x, 1 − y, −z). The dimeric aggregates are linked into a chain via π–π interactions akin to that shown in Fig. 5a. The difference occurs in that C–H⋯S interactions in 3 now fall beneath the distance threshold for such interactions [64]; Table 3, and serve to link the chains into a two-dimensional array in the bc-plane, Fig. 7.

Linear supramolecular chains along the c-axis are found in the crystal structure of 4 stabilised by the bifurcated aromatic-C15–H atom which forms C15–H⋯S4 and C15–H⋯π(CdS3S4C4) interactions as described for 2. Table 3. The minimal difference is that the additional C–H⋯S interaction observed in 2 to link molecules into a 31 helix are beyond the accepted distance threshold in 4 [64], i.e. C3–H⋯S2 = 2.90 Å; the π–π interactions persist, Table 3. In the crystal structure of 5, with the bulkiest xanthate-bounds substituent, the only supramolecular synthons to persist are C17–H⋯π(CdS3S4C4) interactions, Table 3, that stabilise the supramolecular chain along the c-axis, Fig. 8. The oxo atom is directed away from the remaining part of the molecule but a short S1⋯O3 contact of 3.162(5) Å, cf. the sum of their van der Waals radii of 3.32 Å [68], is noted.

![Fig. 4. Molecular structures of (a) Cd(S2COME)2(dafone) (3), (b) Cd(S2COEt)2(dafone) (4), and (c) Cd(S2CO-iPr)2(dafone) (5).](image-url)
3.3 Discussion

As observed above, systematic differences in the mode of coordination of the dafone ligand are noted in that when the C¼O interactions are evident, an asymmetric mode of coordination is found. This is correlated with the coordinating ability of the dafone ligand as discussed below.

While patently less well studied than their 2,2'-bipyridine counterparts, structural studies of the dafone molecule indicate that the latter is a less potent chelating ligand than 2,2'-bipyridine, an observation correlated with the electron-withdrawing ketone group. A survey of the Cambridge Structural Database (CSD) [69] revealed 37 neutral and non-polymorphic metal complexes featuring the dafone molecule coordinating in one of several ways such as chelating, asymmetrically chelating or even monodentate modes as well as single examples each of an $\eta^4$ fashion employing four of the carbon atoms of the five-membered ring (excluding the ketone-carbon) [70] and a bidentate bridging mode [71]. A complementary survey of the CSD revealed over 6000 transition metal complexes containing 2,2'-bipyridine and of these, there were only three examples of monodentate coordination, [72] two examples of bidentate bridging in isolated species [73, 74] and seven examples of bidentate bridging in polymeric species [75–80]; see Supplementary material Table S1 for details.
There are two dafone structures particularly worthy of highlighting.

The first striking structure highlighting the differing coordinating abilities of 2,2'-bipyridine and dafone is that of Pt(dafone)(DMSO)Cl$_2$ [81] where the DMSO molecule coordinates via the sulphur atom and the dafone ligand is monodentate (Pt–N = 2.024(4) and 3.085(4) Å). By comparison, in all other platinum(II) complexes with bipyridine-type ligands, these are chelating [69]. The second remarkable structure is that of Zn(dafone)Cl$_2$ (OH$_2$), where in the presence of coordinated water a monodentate mode of coordination for dafone is observed (Zn–N = 2.0933(12) and 3.4267(13) Å) [81]. In 2,2'-bipyridine chemistry, a related structure with O-bound DMSO is known, Zn(2,2'-bipyridine)Cl$_2$(DMSO), but 2,2'-bipyridine is chelating (Zn–N = 2.1546(16) and 2.1603(16) Å) within a penta-coordinate geometry [82].

There are three pairs of directly comparable dafone- and 2,2'-bipyridine-containing structures where the magnitude of the M–N bond lengths may be assessed, namely PdLCl$_2$ [83–85], cis-NiL$_2$(NCS) [86, 87] and Ph$_2$SnLCl$_2$ [88–90]. As seen from Table S2 (Supplementary material), in each case, the M–N bond distances formed by the dafone ligand are both systematically and significantly longer than those formed by 2,2'-bipyridine. Finally, note is made of an intriguing sub-set of dafone-containing structures featuring non-coordinating dafone which instead forms hydrogen N...H–N bonds to coordinated thiourea molecules in the structures of Cu[S=C(NH$_2$)$_2$]Cl(dafone)H$_2$O [91], M[S=C(NH$_2$)$_2$]Cl$_2$(dafone)$_n$ for M = Fe ($n$ = 1) [92], Co ($n$ = 2) [93] and Zn ($n$ = 2) [94], and Hg[S=C(NH$_2$)$_2$]Cl$_2$(dafone)$_2$ [95]. No analogous structural chemistry is known for 2,2'-bipyridine [69].

In summary, dafone is a poorer ligand for metal centres than 2,2'-bipyridine. As dafone is a poorer ligand, forming weaker M–N bonds, these will be more susceptible to outside forces, such as intermolecular forces, which in turn will influence the mode of coordination even further.

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Fig. 6. Crystal packing for Zn(S$_2$COEt)$_2$(dafone) (2): Side-on (a) and end-on (b) views of the supramolecular chain in the crystal structure of (2) mediated by C–H...S and C–H...π(chelate) interactions shown as blue and purple dashed lines, respectively. Hydrogen atoms not participating in intermolecular interactions have been omitted for reasons for clarity; and (c) A view in projection down the c-axis of the unit cell contents for (2). The π...π interactions are shown as purple dashed lines.
An example of this is found in the aforementioned \( \text{Ph}_2\text{SnLCl}_2 \) structures [88–90]. In the tetragonal polymorph of \( \text{Ph}_2\text{Sn}(2,2'\text{-bipyridine})\text{Cl}_2 \) [87], centrosymmetrically related molecules associate via \( \pi \ldots \pi \) interactions involving the pyridyl rings as shown in Fig. S1a (Supplementary material); both pyridyl rings in the monoclinic polymorph do not form comparable \( \pi \ldots \pi \) interactions [89]. Accordingly, the Sn–N bond distances in these structures are near symmetric, Table S2 (Supplementary material). In the structure of \( \text{Ph}_2\text{Sn(dafone)Cl}_2 \) [90], one of the pyridyl rings forms a \( \pi \ldots \pi \) interaction with a tin-bound phenyl ring to generate a supramolecular chain, Fig. S1b (Supplementary material). So, while there is no inherent chemical reason for the disparity in the Sn–N bond lengths in this structure, the pyridyl ring participating in the intermolecular interaction association is rendered less basic and therefore forms the longer Sn–N bond (Table S2, Supplementary material). In the structures

Fig. 7. A view of the supramolecular array in the bc-plane in the structure of \( \text{Cd(S}_2\text{COCH}_3)_2\text{(dafone)} \) (3) mediated by C=O...C=O, C–H...S and \( \pi \ldots \pi \) interactions shown as orange, blue and purple dashed lines, respectively. Hydrogen atoms not participating in intermolecular interactions have been omitted for reasons for clarity.

Fig. 8. Side-on (a) and end-on (b) views of the supramolecular chain in the crystal structure of \( \text{Cd(S}_2\text{CO-iPr}_2\text{(dafone)} \) (5) mediated by C–H...\( \pi \) (chelate) interactions shown as purple dashed lines. Hydrogen atoms not participating in intermolecular interactions have been omitted for reasons for clarity.
of 1 and 3, the pyridyl ring associated with the longer Zn–N and Cd–N bond lengths also participates in a π...π interaction, resulting in disparate M–N bond lengths, consistent with the above.

An evaluation of the crystal packing patterns of the aforementioned 37 structures showed that two primary modes of association between dafonene molecules exist. These are π...π interactions between the constituent rings: five-membered and pyridyl rings, and between pyridyl rings, and between C=O and five-membered or pyridyl rings. No evidence for C=O...C=O interactions in the literature dafonene structures was found indicating that the mode of supramolecular association observed in 1 and 3 are the first such examples for this class of compound.

Finally, a comment on the isostructural crystal structures of 2, 4 and 5 is warranted. Based on the distance criterion alone [64], different supramolecular architectures can be assigned. Thus, in 2, a helical assembly comprising three chains and sustained by a combination of C–H...S and C–H...π(ZnS3S4C4) and π...π interactions is found. In 4, one C–H...S interaction does not persist so that the helical assemblies no longer form but the π...π interactions remain. Finally, in 5, only the C–H...π(CdS3S4C4) interaction remains, leading to supramolecular chains. The fact that all three crystal packing patterns are the same points to the importance of global crystal packing of the molecules rather than individual (weak) synths [42] the persistence of the C–H...π(chelate) interactions notwithstanding. This point is also borne out in the crystal structures of 1 and 3 where a C–H...S interaction in 3 leads to a two-dimensional array, whereas in the “absence” of this contact in 1, the supramolecular assembly is based on a chain.

To close this discussion, it is apposite to reconsider the bifurcated C15–H...S3 and C–H...π(ZnS3S4C4) interactions leading to a linear supramolecular in the crystal structure of 2 (Table 3), suggesting these interact cooperatively. The interpretation of geometric parameters describing weak intermolecular interactions is dangerous as their inherently weak nature implies that they have a greater susceptibility to external forces [27, 96]. In the case of the aforementioned bifurcated interaction, the H...S distance is longer than the H...π(chelate) separation; both sulphur and an arene ring are assumed to have the comparable van der Waals radii [27]. This being stated, the C–H...S interaction angle is closer to 180°, by 24° compared with the C–H...π(ZnS3S4C4) contact. The persistence of the C–H...π(ZnS3S4C4) across the series points to its relative importance of the two interactions in the present series of structures.

The clear difference between the crystal packing is found in the presence of C=O...C=O interactions so that in 1 and 3, the crystal structures can be considered as essentially close-packing of binuclear aggregates whereas in 2, 4 and 5, the crystal structures can be considered as the close-packing of mononuclear aggregates. As such, it is not surprising that the tighter interactions in 1 and 3 are reflected in the Kitagorodsky’s packing index (as calculated in PLATON [64]) of 70.3 and 70.1%, respectively, values higher than 67.6, 67.1 and 68.3% for 2, 4 and 5, respectively [97].

4. Conclusions

With the smaller xanthate-bound methyl groups in 1 and 3, anti-parallel C=O...C=O interactions are formed in their crystal structures. The dimeric aggregates thus produced are associated via π...π interactions into a supramolecular chain, and then in the case of 3 into a two-dimensional array via C–H...S contacts. Increasing the size of the organic residue, i.e. to ethyl and isopropyl, does not allow for the formation of this supramolecular architecture. Instead, supramolecular chains are sustained by C–H...S and C–H...π(chelate) interactions (the latter exclusively in the case of 5). Regardless of the presence of identifiable π...π and C–H...S and C–H...π(chelate) contacts, the crystal structures of isomorphous 1 and 3 may be considered as close-packing of binuclear aggregates whereas the crystal structures of 2, 4 and 5, with no strong intermolecular interactions at play, may be considered as close-packing of mononuclear species.

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References

[97] The calculated Kitaigorodsky’s packing index cited for each of 4 and 5 are overestimates owing to disorder in the resides which, for the purposes of calculation were each assigned full weights. For calculations performed on 4 assuming full weight for the major component of the disorder (0.76(3)) the value was calculated at 65.1%; assuming full weight for the minor component gave 65.2%. For 5, where two orientations of equal weight were resolved, assuming full weight for either of these returned values of 65.9 and 66.0%.