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Emerging supramolecular synthons: C–H⋯π(chelate) interactions in metal bis(1,1-dithiolates)†

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Crystal structures of transition and main group element 1,1-dithiolates are shown to be partially sustained by C–H⋯π(chelate) interactions. For the planar binary bisdithiocarbamates, C–H⋯π(MS₂C) interactions lead to aggregation patterns ranging from a 0-D four molecule aggregate to a 3-D architecture but with the majority of structures featuring 1-D or 2-D supramolecular assemblies.

While the pivotal role of conventional hydrogen bonding interactions in crystal engineering is widely acknowledged, in situations where hydrogen bonding does not extend in three dimensions or does not exist, owing to a lack of appropriate acceptors/donors, there is a clear demand to determine the nature of other types of intermolecular interactions contributing to the stability of a crystal structure.† Of what might be termed second tier supramolecular synthons, interactions of the type π⋯π and C–H⋯π, where the π-system is typically an aryl ring, are now well established in crystal engineering. In the domain of metalorganic crystal engineering, the metalloaromatic character of chelate rings‡ gives rise to the possibility of alternative π-systems. Indeed, systematic evaluation by Zaric et al. of π(chelate)⋯π(chelate) stacking interactions occurring in neutral square planar transition metal complexes revealed that in almost 40% of structures these did in fact occur and when present these interactions cooperate.5 The π(chelate)⋯π(chelate) interactions have features in common with those of all organic systems such as distance of separation and orientation, e.g. parallel and anti-parallel. Mixed π(aryl)⋯π(chelate) interactions have also been noted.6 In the same way, C–H⋯π(chelate) synthons have precedents in the literature.

In a literature-based evaluation, again by Zaric et al., of C–H⋯π interactions occurring between square planar transition metal acetylacetonate (acac) complexes and phenyl rings revealed that the chelate ring could function as an acceptor, i.e. participate in phenyl-C–H⋯π(chelate) interactions, as well as a donor, i.e. forming acac-C–H⋯π(phenyl) interactions. The energies of association afforded by C–H⋯π(chelate) interactions were estimated6 to be in the range 6–11 kJ mol⁻¹ which is comparable to 1–8 kJ mol⁻¹ for organic systems.7 Otherwise, comment upon C–H⋯π(chelate) interactions appears to be sporadic and limited to individual papers.8 A notable exception, and relevant to the present contribution, are C–H⋯π(chelate = MS₂C) synthons highlighted in the supramolecular chemistry of metal xanthates,8c see Fig. 1 for chemical structures of the 1,1-dithiolate ligands discussed herein. Prompted by the above, it was thought of interest to assess the propensity of metal (1,1-dithiolates) to participate in C–H⋯π(chelate) interactions. In particular it was desirable to determine whether the metal dithiocarbamates, ubiquitous in the crystallographic literature, would be more likely to form such interactions, owing to the relatively high contribution of canonical structure (f) (Fig. 1) leading to more efficient electron delocalisation over the chelate ring.

The CSD was searched using CONQUEST9 with the following structural protocols described here for dithiocarbamate structures. Referring to the data in Table 1, “All structures” were retrieved with no restrictions as long as one dithiocarbamate ligand was present. Structures were then sorted in accord with the following groupings: those containing a transition metal ligand was present. Structures were then sorted in accord with the following groupings: those containing a transition metal (incorporating the zinc triad elements), a main group element, and containing lanthanide or actinide elements. Additional search criteria were then applied in accord with those illustrated in Fig. 2. Thus, examples with values of z less than 20°, β in the range 110 to 180°, and d₁ within 2.4 to 3.6 Å were retrieved as they

![Generic structures for the 1,1-dithiolate ligands discussed herein](image)

**Fig. 1** Generic structures for the 1,1-dithiolate ligands discussed herein: (a) xanthate (dithiocarbonate), (b) dithiocarbamate, (c) dithiophosphate, (d) dithiophosphinate, and (e) dithiophosphinate. R = alkyl and/or aryl and may be different to each other. (f) Prominent canonical structure for the dithiocarbamate ligand.

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† Electronic supplementary information (ESI) available: Data for and diagrams illustrating C–H⋯π(chelate) interactions in planar metal bisdithiocarbamates (24 pages). See DOI: 10.1039/c1cc11173f
were considered most likely to feature at least one C–H···π(chelate) interaction contributing to the stabilisation of the crystal structure in a given dimension. The data in Table 1 indicate that C–H···π(chelate) interactions do apparently exist in the crystal structures of metal 1,1-dithiolates. Being entirely consistent with the relative high contribution of canonical structure (f) to their structures, metal dithiocarbamates show a greater likelihood of forming these types of interactions, in both their transition and metal group element complexes, than metal xanthates, and that the probability of forming these in metal dithiophosphates, dithiophosphonates and dithiophosphinates falls off significantly. The final general observation is that transition metal complexes are more likely to form C–H···π(chelate) interactions than their main group metal element counterparts, an observation that readily correlated with the symmetric mode of coordination often seen in transition metal complexes.

In order to achieve a manageable number of structures to carefully analyse, an additional criterion was added in that planar coordination often seen in transition metal complexes. For Ni(S2CN(Et)Cy)2,11 each centrosymmetric molecule forms two donor and two acceptor interactions to form a one dimensional chain with a linear topology. This example does not imply that only small N-bound residues allow C–H···π(MS2C) interactions. In contrast, a similar arrangement is found in the Pt structure with an aza-15-crown-5-dithiocarbamate.11d Each of the molecules adopting this motif is centrosymmetric with the simple variation being the number of contacts between molecules; two chains of the 12 feature molecules participating in four C–H···π(MS2C) interactions. The predominant supramolecular motif is a 2-D array, adopted by 21 examples, whereby each molecule is surrounded by four others. As exemplified in Fig. 3(d) for Ni(S2CN(Et)Cy)2,11c each centrosymmetric molecule forms two donor and two acceptor interactions to form a 2-D layer with a flat topology. As with the supramolecular chain motif, all 2-D arrays feature centrosymmetric molecules and the variation is found in the number of C–H···π(MS2C) contacts formed per molecule with the majority forming four; there are six examples forming eight interactions.

With reference to the main group bis(dithiocarbamate)s, there is one example of a supramolecular chain but sustained by two C–H···π(MS2C) interactions only, five examples of 2-D arrays, resembling that shown in Fig. 3(d), with three sustained by four interactions, one sustained by six and one sustained by eight C–H···π(MS2C). The remaining structure adopts a fifth structural motif and involves solvent benzene as the C–H donor. As illustrated in Fig. 3(e) for Se(S2CNEt2)2C6H6,11f with the Se atom situated on a two-fold axis and the benzene

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**Table 1** Frequency of C–H···π(chelate) interactions occurring in neutral metal complexes having at least one 1,1-dithiolate ligand

<table>
<thead>
<tr>
<th>1,1-Dithiolate ligand</th>
<th>All structures</th>
<th>Structures with C–H···π(chelate)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TR</td>
<td>MG</td>
</tr>
<tr>
<td>A. S2CNR2</td>
<td>1467</td>
<td>622</td>
</tr>
<tr>
<td>B. S2COR</td>
<td>287</td>
<td>123</td>
</tr>
<tr>
<td>C. S2P(OR)2</td>
<td>573</td>
<td>123</td>
</tr>
<tr>
<td>D. S2P(OR)(R')</td>
<td>68</td>
<td>19</td>
</tr>
<tr>
<td>E. S2PR2</td>
<td>58</td>
<td>102</td>
</tr>
</tbody>
</table>

*See Fig. 1 for generic structures. Abbreviations employed: TR = any transition metal; MG = any element of the Al to Tl group, Si to Pb, P to Bi, and S to Te; LN = any lanthanide; AN = any actinide. *Number of examples of metal complexes having at least one 1,1-dithiolate ligand. *Number of examples having evidence for a C–H···π interaction according to the stated search criteria.

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**Fig. 2** Search protocols for C–H···π(chelate) interactions (illustrated for dithiocarbamate structures): d1 is the distance between the ring centroid of the chelate ring (Cg) and the H atom; V2 is the vector normal to the plane through the MS2C chelate ring; z is the angle between the d1 and V2 vectors, and β is the C–H···Cg angle.
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in cases where the interactions under consideration are weak, especially in consideration of the lack of precision in the location of hydrogen atoms in crystallographic studies.

A survey of the crystallographic literature of metal 1,1-thiolates shows that their crystal structures are often sustained by C–H⋅⋅⋅π(chelate) interactions. For example, square planar transition metal and trapezium main group element dithiocarbamate complexes exhibit such interactions in nearly 40% of their crystal structures. Clearly, C–H⋅⋅⋅π(chelate) interactions play an important role in stabilising these and the crystal structures of other metalorganics. Placed in context, the eight-membered carboxylate dimer {⋯····HOC=O⋯}₂ synthon occurs in approximately 33% of their organic crystal structures.³³ Contrasting the two synths, it is likely that most analyses would naturally include a search for the {⋯····HOC=O⋯}₂ synthon when this synthon can potentially form. However, it is likely that the opposite is true for C–H⋅⋅⋅π(chelate) interactions, despite the fact that these are often indicated in the PLATON listings.¹¹α

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Notes and references


molecule disposed about a centre of inversion, supramolecular chains of Se(S₂CNEt₂)₂ are sustained by two donor and two acceptor C–H⋅⋅⋅π(SeS₂C) interactions, analogous to that shown in Fig. 3(c), with the chains linked by benzene-C–H⋅⋅⋅π(SeS₂C) interactions to form a 2-D array with a flat topology. All of the transition metals that are known to form square planar bisdithiocarbamate structures also provide examples that feature C–H⋅⋅⋅π(MS₂C) interactions in their crystal structures. In order of prevalence, Ni (14 examples out of 32 possible structures), Cu (11/18), Pd (7/14), Pt (2/5) and Hg (1/2); for main group elements: Te (5/9) and Se (2/4). Finally, as noted previously,¹² distance/angle correlations are problematic in cases where the interactions under consideration are weak.

Fig. 3 Representative examples of supramolecular aggregation sustained by C–H⋅⋅⋅π(chelate) interactions in square planar transition metal and trapezium main group element geometries: (a) isolated 0-D four molecule aggregate in the crystal structure of Pd[S₂CN(CH₂Ph)₂]₂, (b) 3-D architecture in Pd[S₂CN(n-Bu)Me₂], (c) supramolecular chain in Cu[S₂CN(CH₂CH₃)Cy]₂, (d) 2-D array in Ni[S₂CN(CH₂CH₃)Cy]₂ and (e) solvent-mediated 2-D array in Se(S₂CNEt₂)₂-C₆H₆.