Supramolecular Association via Hg···S Secondary-Bonding Interactions in Crystals of Organomercury(II) Species: A Survey of the Cambridge Structure Database

Edward R.T. Tiekink

Research Centre for Crystalline Materials, School of Medical and Life Sciences, Sunway University,
Badar Sunway 47500, Selangor Darul Ehsan, Malaysia; edwardt@sunway.edu.my; Tel.: +60-374917181

SUPPLEMENTARY MATERIALS

1. Zero-dimensional aggregates featuring Hg···S secondary-bonding interactions.

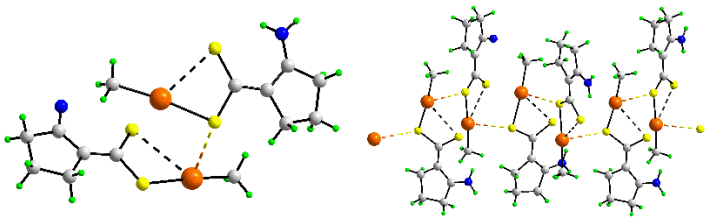

Figure S1. IHOLEW (2-Aminocyclopent-1-ene-1-carbodithioato)-methyl-mercury(II) [39]

d(Hg···S) = 3.328(3) Å; Hg–S···Hg = 97.35(8)°; C–S···Hg = 119.9(3)°

S–Hg···S = 85.76(7)°; C–Hg···S = 98.3(3)°

{Two independent molecules comprise the asymmetric unit which are connected by a Hg···S interaction. Intramolecular Hg···S contacts are noted with Hg···S = 3.080(2) and 3.163(3) Å; the second, longer value involves the Hg atom forming the intermolecular contact. Another Hg···S interaction beyond the van der Waals distance criterion is noted (Hg···S = 3.362(2) Å which connects the dimers into a twisted, supramolecular chain. See IHOLEW01 (**57**) for a polymorphic crystal}

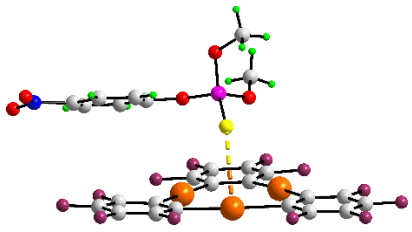

Figure S2. CEJNUB tris(μ_2-Perfluoro-o-phenylene)-tri-mercury bis(dimethyl(4-nitrophenyl)-thiophosphate) [38].

d(Hg···S) = 3.278(5) Å; C–S···Hg = 86.1(3) & 90.4(3)°

P–Hg···S = 154.3(2)°

{Two co-formers of the 1:2 co-crystal assemble into a zero-dimensional aggregate. If the van der Waals criterion was relaxed, the sulphur atom might be considered μ_3-bridging with the additional Hg···S separations being 3.399(3) and 3.428(3) Å. Indeed, the sulphur atom of the second molecule forms three similar contacts to the other side of the triangular face with Hg···S = 3.375(3), 3.411(4) & 3.651(5) Å}

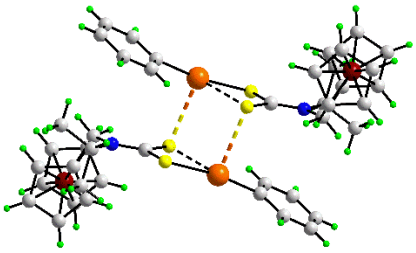

Figure S3. FUPFEC ((N-Isopropyl-N-(ferrocenyl)methyl)dithiocarbamato)-phenyl-mercury [40]

d(Hg···S) = 3.0773(13) Å; C–S···Hg = 90.33(16)°

S–Hg···S = 89.24(4)°; C–Hg···S = 99.81(13)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.9025(7) Å is noted}

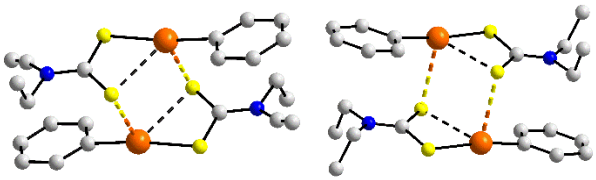

Figure S4. FOKBIQ Phenyl-(diethylthiocarbamato)-mercury(II) [41]

d(Hg···S) = 3.133(3) Å; C–S···Hg = 92.8(3)°

S–Hg···S = 91.01(8)°; C–Hg···S = 96.7(3)°

d(Hg···S) = 3.191(3) Å; C–S···Hg = 86.7(3)°

S–Hg···S = 91.13(8)°; C–Hg···S = 97.4(3)°

{Two independent molecules. Each molecule associates about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact in each molecule is noted = 2.978(2) and 2.923(3) Å}

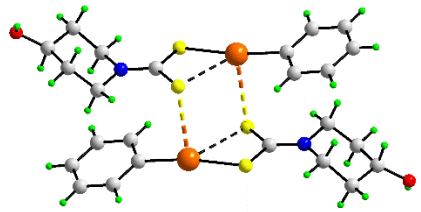

Figure S5. LUWZOU (4-Hydroxypiperidine-1-carbodithioato)-phenyl-mercury(II) chloroform solvate [42].

d(Hg···S) = 3.145(2) Å; C–S···Hg = 92.9(3)°

S–Hg···S = 90.77(7)°; C–Hg···S = 95.9(3)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 3.016(3) Å is noted}

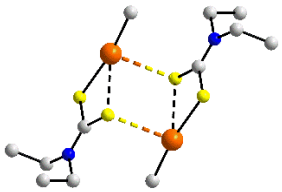

Figure S6. MEDTHG Methyl-(N,N-diethyldithiocarbamato)-mercury(II) [43]

d(Hg···S) = 3.148(8) Å; C–S···Hg = 98.8(8)°

S–Hg···S = 90.2(2)°; C–Hg···S = 96.9(5)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.963(8) Å is noted}

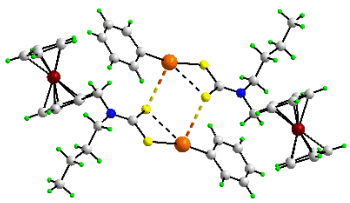

Figure S7. FUPFIG ((N-butyl-N-(ferrocenyl)methyl)dithiocarbamato)-phenyl-mercury(II) [40].

d(Hg···S) = 3.161(5) Å; C–S···Hg = 99.3(6)°

S–Hg···S = 92.50(13)°; C–Hg···S = 97.8(5)°

{The molecule associates about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact in each molecule is noted = 2.954(5) Å}

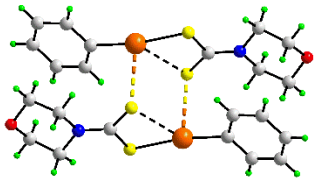

Figure S8. YOLJAL (Morpholinedithiocarbamato)-phenyl-mercury(II) [44]

d(Hg···S) = 3.1727(13) Å; C–S···Hg = 90.01(17)°

S–Hg···S = 91.81(4)°; C–Hg···S = 98.17(13)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.9725(13) Å is noted}

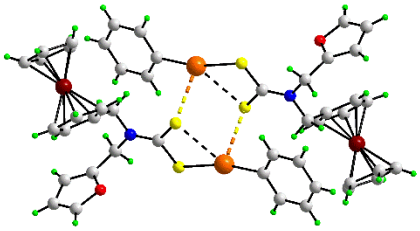

Figure S9. EKIYUT Phenyl-((furan-2-ylmethyl(ferrocenylmethyl)amino)dithiocarbamato)-mercury(II) [45].

d(Hg···S) = 3.174(3) Å; C–S···Hg = 94.6(4)°

S–Hg···S = 89.94(7)°; C–Hg···S = 99.6(3)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.981(2) Å is noted}

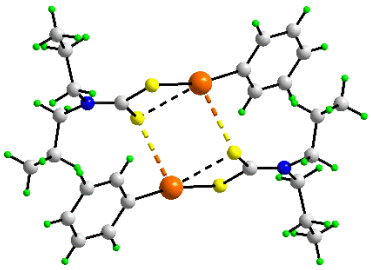

Figure S10. GUVQUJ Phenyl-(N,N-di-n-propyldithiocarbamato-S,S')-mercury(II) [46].

d(Hg···S) = 3.1809(9) Å; C–S···Hg = 93.54(13)°

S–Hg···S = 90.54(3)°; C–Hg···S = 97.28(10)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.9093(12) Å is noted}

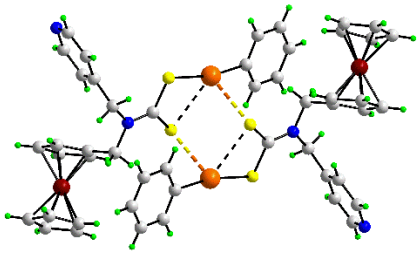

Figure S11. EKIYON Phenyl-((ferrocenylmethyl(4-pyridinylmethyl)amino)dithiocarbamato)-mercury(II) [45].

d(Hg···S) = 3.181(3) Å; C–S···Hg = 98.5(4)°

S–Hg···S = 93.27(9)°; C–Hg···S = 95.5(3)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.958(3) Å is noted}

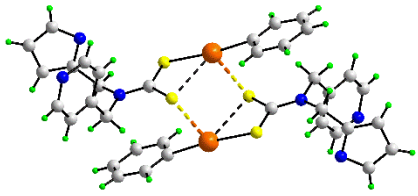

Figure S12. FODRUN (N-(4-Pyridylmethyl)-N-(pyrrol-2-yl)dithiocarbamato-S,S')-phenyl-mercury(II) methanol solvate [47].

d(Hg···S) = 3.191(5) Å; C–S···Hg = 88.8(5)°

S–Hg···S = 92.87(13)°; C–Hg···S = 92.1(4)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 3.020(5) Å is noted}

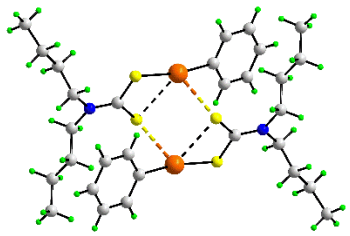

Figure S13. YOLHUD (Di-n-butyldithiocarbamato)-phenyl-mercury(II) [44].

d(Hg···S) = 3.2179(18) Å; C–S···Hg = 98.5(2)°

S–Hg···S = 94.03(6)°; C–Hg···S = 93.1(2)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.9465(19) Å is noted}

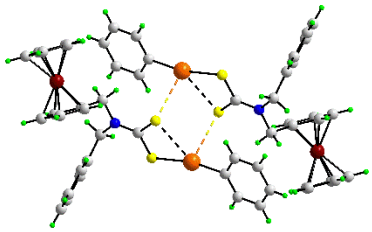

Figure S14. FUPFAY ((N-benzyl-N-(ferrocenyl)methyl)dithiocarbamato)-phenyl-mercury(II) [40].

d(Hg···S) = 3.230(2) Å; C–S···Hg = 96.5(3)°

S–Hg···S = 92.02(7)°; C–Hg···S = 96.9(2)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.965(2) Å is noted}

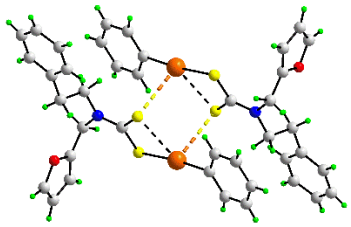

Figure S15. NEGRID (N-furfuryl-N-(2-phenylethyl)dithiocarbamato-S,S')-phenyl-mercury(II) [48].

d(Hg···S) = 3.2479(15) Å; C–S···Hg = 93.80(18)°

S–Hg···S = 91.65(4)°; C–Hg···S = 92.53(14)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 2.9026(15) Å is noted}

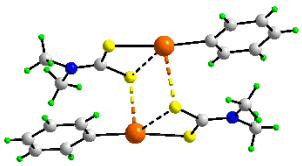

Figure S16. HEGGOS (dimethylcarbamodithioato)-phenyl-mercury(II) [49].

d(Hg···S) = 3.251(2) Å; C–S···Hg = 87.8(2)°

S–Hg···S = 87.8(7)°; C–Hg···S = 99.2(2)°

d(Hg···S) = 3.341(2) Å; C–S···Hg = 87.1(2)°

S–Hg···S = 94.65(6)°; C–Hg···S = 92.9(2)°

{There are two independent molecules in the asymmetric unit and these associate via a pair of Hg···S interactions to form a zero-dimensional aggregate. Intramolecular Hg···S contacts are noted, i.e., 2.939(2) and 3.011(2) Å is noted}

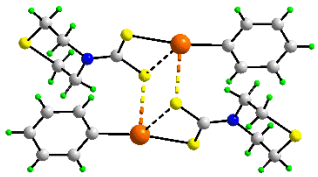

Figure S17. YOMXUV Phenyl-(thiomorpholine-4-carbodithioato)-mercury(II) [50].

d(Hg···S) = 3.252(4) Å; C–S···Hg = 93.2(6)°

S–Hg···S = 92.47(14)°; C–Hg···S = 95.6(5)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. An intramolecular Hg···S contact of 2.998(5) Å is noted}

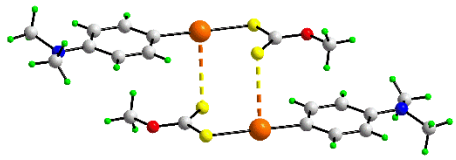

Figure S18. LAJGOV (4-(Dimethylamino)phenyl)-(O-methyl carbonodithioato)-mercury [51].

d(Hg···S) = 3.2649(15) Å; C–S···Hg = 93.67(16)°

S–Hg···S = 86.99(4)°; C–Hg···S = 93.45(16)°

{The molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact = 3.1128(14) Å is noted}

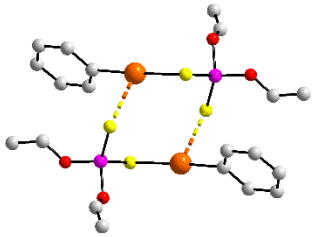

Figure S19. YAHFIW (Diethyldithiophosphate)-phenyl-mercury(II) [52].

d(Hg···S) = 3.325(6) Å; P–S···Hg = 93.6(3)°

S–Hg···S = 83.60(17)°; C–Hg···S = 100.4(4)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate}

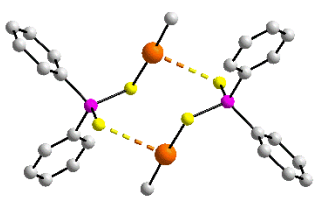

Figure S20. VIHCUK Methyl-(diphenyldithiophosphinate)-mercury(II) [53].

d(Hg···S) = 3.152(3) Å; P–S···Hg = 92.88(11)°

S–Hg···S = 84.67(8)°; C–Hg···S = 97.0(3)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate}

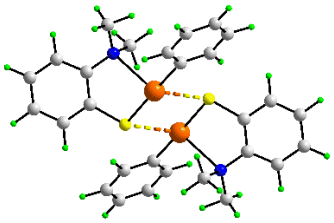

Figure S21. BEBLUP 2-Dimethylaminothiophenolato-phenyl-mercury(II) [55].

d(Hg···S) = 3.224(2) Å; Hg–S···Hg = 94.55(5)°; C–S···Hg = 127.7(2)°

S–Hg···S = 85.45(6)°; C–Hg···S = 94.91(19)°

{H atoms added by Mercury. Centrosymmetrically related molecules assemble into a dimeric aggregate. Intramolecular d(Hg···N) = 2.657(6) Å}

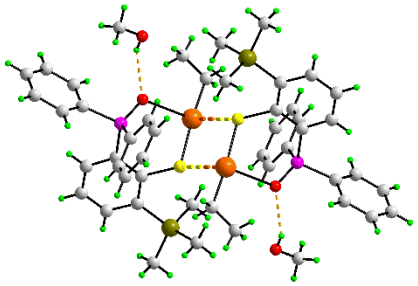

Figure S22. VIYLAR Ethyl-((hydroxy-O)(diphenyl)(2-(sulfanyl-S)-3-(trimethylsilyl)phenyl)-phosphoniumato)-mercury methanol solvate [56].

d(Hg···S) = 3.2498(11) Å; Hg–S···Hg = 103.08(3)°; C–S···Hg = 142.26(12)°

S–Hg···S = 76.92(3)°; C–Hg···S = 102.34(19)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. Intramolecular d(Hg···O) = 2.712(4) Å. Methanol-O–H···O(oxide) hydrogen bonds are shown as orange dashed lines}

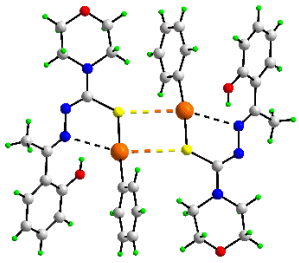

Figure S23. BORCIV (N-(1-(2-Hydroxyphenyl)ethylidene)-4-morpholinecarbohydrazonothioato-S)-(phenyl)-mercury [59].

d(Hg···S) = 3.250(2) Å; Hg–S···Hg = 90.33(6)°; C–S···Hg = 148.0(3)°

S–Hg···S = 90.61(6)°; C–Hg···S = 83.4(2)°

d(Hg···S) = 3.289(2) Å; Hg–S···Hg = 89.26(6)°; C–S···Hg = 146.6(3)°

S–Hg···S = 89.79(6)°; C–Hg···S = 89.78(19)°

{Two independent molecules associate to form a dimeric aggregate. Intramolecular d(Hg···N) = 2.801(7) Å and d(Hg···N) = 2.862(7) Å}

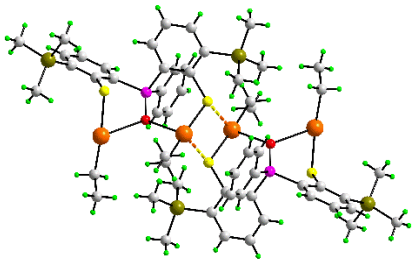

Figure S24. VIYLIZ (μ_2-bis(3-Trimethylsilylphenyl-2-thiolato)phenyl(oxo)phosphanyl-S,S)-diethyl-di-mercury(II) [56].

d(Hg···S) = 3.256(2) Å; Hg–S···Hg = 106.86(7)°; C–S···Hg = 136.92(2)°

S–Hg···S = 73.14(6)°; C–Hg···S = 108.7(3)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. The Hg···O separations are 2.700(4) and 2.748(6) Å for the endo- and exo-cyclic contacts, respectively}

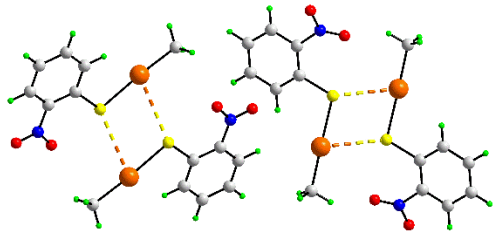

Figure S25. NEFDEH Methyl-(2-nitrobenzenethiolato)-mercury(II) [58].

d(Hg···S) = 3.257(4) Å; Hg–S···Hg = 105.61(14)°; C–S···Hg = 130.3(3)° {right-hand dimer}

S–Hg···S = 74.39(13)°; C–Hg···S = 103.4(6)°

d(Hg···S) = 3.321(4) Å; Hg–S···Hg = 107.25(14)°; C–S···Hg = 131.2(3)°

S–Hg···S = 72.75(13)°; C–Hg···S = 103.7(4)°

{Two independent molecules. Centrosymmetrically related molecules assemble into a dimeric aggregate}

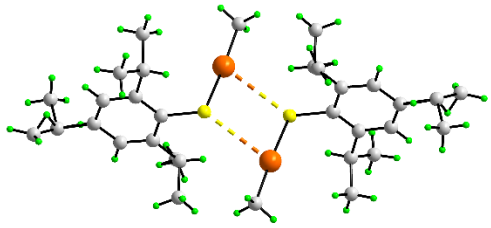

Figure S26. JETYEM Methyl-(2,4,6-tri-isopropylbenzenethiolato)-mercury(II) [59].

d(Hg···S) = 3.269(4) Å; Hg–S···Hg = 100.63(13); C–S···Hg = 134.6(4)°

S–Hg···S = 79.37(12)°; C–Hg···S = 104.2(6)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate}

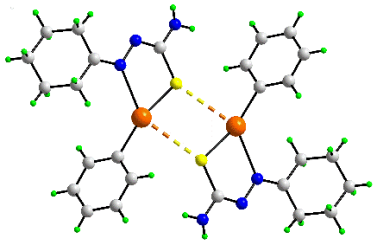

Figure S27. PAVVOY (Cyclohexanone thiosemicarbazonato-N,S)-phenyl-mercury(II) [60].

d(Hg···S) = 3.2758(11) Å; Hg–S···Hg = 102.88(4); C–S···Hg = 150.17(12)°

S–Hg···S = 77.12(3)°; C–Hg···S = 88.04(10)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate; intramolecular d(Hg···N) = 2.526(3) Å}

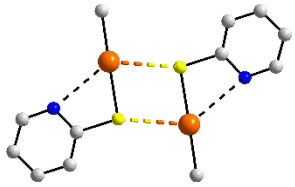

Figure S28. DOMCAJ01 Methyl-(pyridine-2-thiolato-S)-mercury(II) [61].

d(Hg···S) = 3.322(4) Å; Hg–S···Hg = 104.14(11)°; C–S···Hg = 139.9(4)°

S–Hg···S = 75.86(10)°; C–Hg···S = 101.6(3)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. An intramolecular Hg···N contact of 2.981(9) Å is noted}

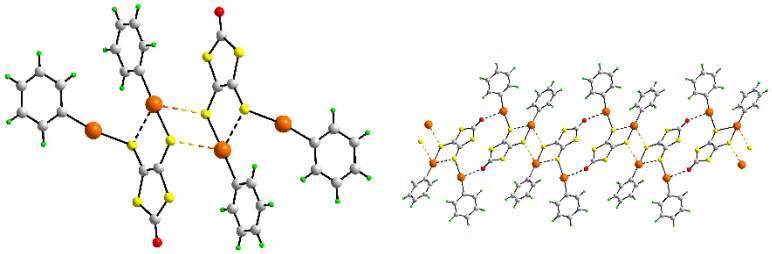

Figure S29. HUBRON bis(μ_2-4,5-Disulfanyl-1,3-dithiol-2-one)-tetraphenyl-tetra-mercury [62].

d(Hg···S) = 3.3014(11) Å; Hg–S···Hg = 95.98(4)°; C–S···Hg = 83.54(16)°

S–Hg···S = 80.02(4)°; C–Hg···S = 101.51(13)°

{The di-nuclear molecules associate about a centre of inversion to form a zero-dimensional aggregate. An intramolecular Hg···S contact of 2.9315(12) Å is noted. Inter-dimer Hg···O(carbonyl) contacts of 2.738(4) Å link the dimers into a linear, supramolecular chain}

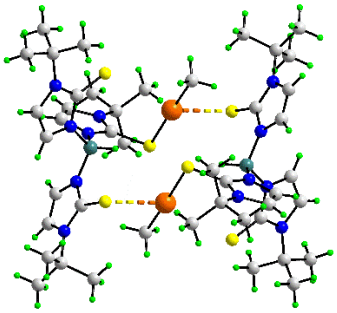

Figure S30. CIJPOB (Hydrogen tris(2-mercapto-1-t-butylimidazolyl)borate-S)-methyl-mercury(II) acetonitrile tetra-solvate [63].

d(Hg···S) = 3.206(2) Å; C–S···Hg = 88.1(2)°

S–Hg···S = 83.05(5)°; C–Hg···S = 96.7(2)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. An additional Hg···S contact is noted involving the third thione-S atom, i.e., 3.347(2) Å}

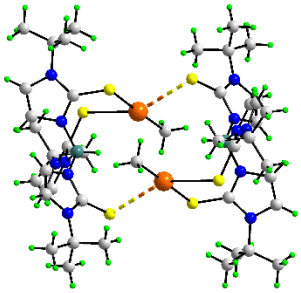

Figure S31. CIJPIV (Hydrogen tris(2-mercapto-1-t-butylimidazolyl)borate-S)-methyl-mercury(II) [63].

d(Hg···S) = 3.2463(15) Å; C–S···Hg = 98.29(17)°

S–Hg···S = 83.03(4)°; C–Hg···S = 93.9(3)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. An additional Hg···S contact is noted involving the third thione-S atom, i.e., 3.285(2) Å}

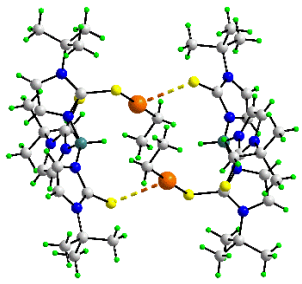

Figure S32. CIJQAO (Hydrogen tris(2-mercapto-1-t-butylimidazolyl)borate-S)-ethyl-mercury(ii) acetone hemi-solvate [63].

d(Hg···S) = 3.2523(6) Å; C–S···Hg = 99.88(7)°

S–Hg···S = 84.542(16)°; C–Hg···S = 93.89(8)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. An intramolecular Hg···S contact of 3.318(6) Å is noted}

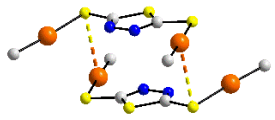

Figure S33. KAPWUT (μ2-1,3,4-Thiadiazole-2,5-dithiolato-S,S')-bis(methyl-mercury(II)) [64].

d(Hg···S) = 3.349(12) Å; Hg–S···Hg = 88.7(3); C–S···Hg = 90(1)°

S–Hg···S = 85.9(4)°; C–Hg···S = 94(2)°

{Centrosymmetrically related molecules assemble into a dimeric aggregate. Additional, weaker Hg···S (3.429(13) Å) interactions occur within the dimer involving the exocyclic mercury atom and the sulphur atom not involved in the endocyclic contact. An intramolecular Hg···N contact (2.93(3) Å) is noted as is an intermolecular Hg···N contact of 2.765(3) Å when all taken together link molecules into a 3D framework}

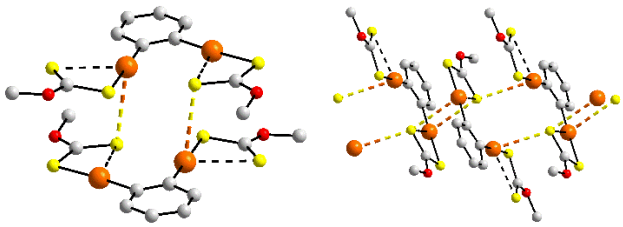

Figure S34. FAZBOX (μ2-o-Phenylene)-bis(O-methyl-xanthato-S)-di-mercury dichloromethane mono-solvate [65].

d(Hg···S) = 3.348(5) Å; C–S···Hg = 99.9(6)°

S–Hg···S = 82.91(15)°; C–Hg···S = 97.7(4)°

{One of the mercury atoms of the di-nuclear molecule forms a Hg···S contact about a centre of inversion. It is noted that the second mercury atom forms a Hg···S contact but marginally outside of the distance criterion, i.e., Hg···S = 3.354(5) Å. Should the latter interaction be taken

into account, a twisted supramolecular chain eventuates, as shown in the right-hand image. Further, there are two intramolecular Hg···S interactions: 3.014(6) and 3.151(6) Å}

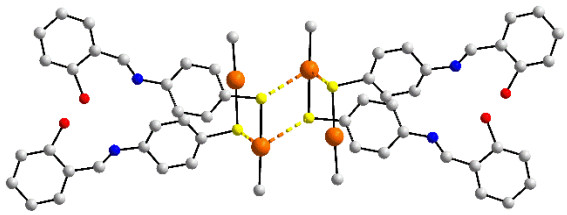

Figure S35. QUGVUJ (4-(o-Hydroxybenzylideneamino)phenylthiolato)-methyl-mercury(ii) [66].

d(Hg···S) = 3.316(8) Å; Hg–S···Hg = 102.2(2)°; C–S···Hg = 137(1)°

S–Hg···S = 77.8(2)°; C–Hg···S = 106(1)°

d(Hg···S) = 3.294(8) Å; Hg–S···Hg = 97.4(2)°; C–S···Hg = 107(1)°

S–Hg···S = 93.1(2)°; C–Hg···S = 90(1)°

{Two independent di-nuclear molecules. One assembles into a dimeric aggregate about a centre of inversion (first entry). The second independent molecule is attached at the periphery to form a four-molecule aggregate}

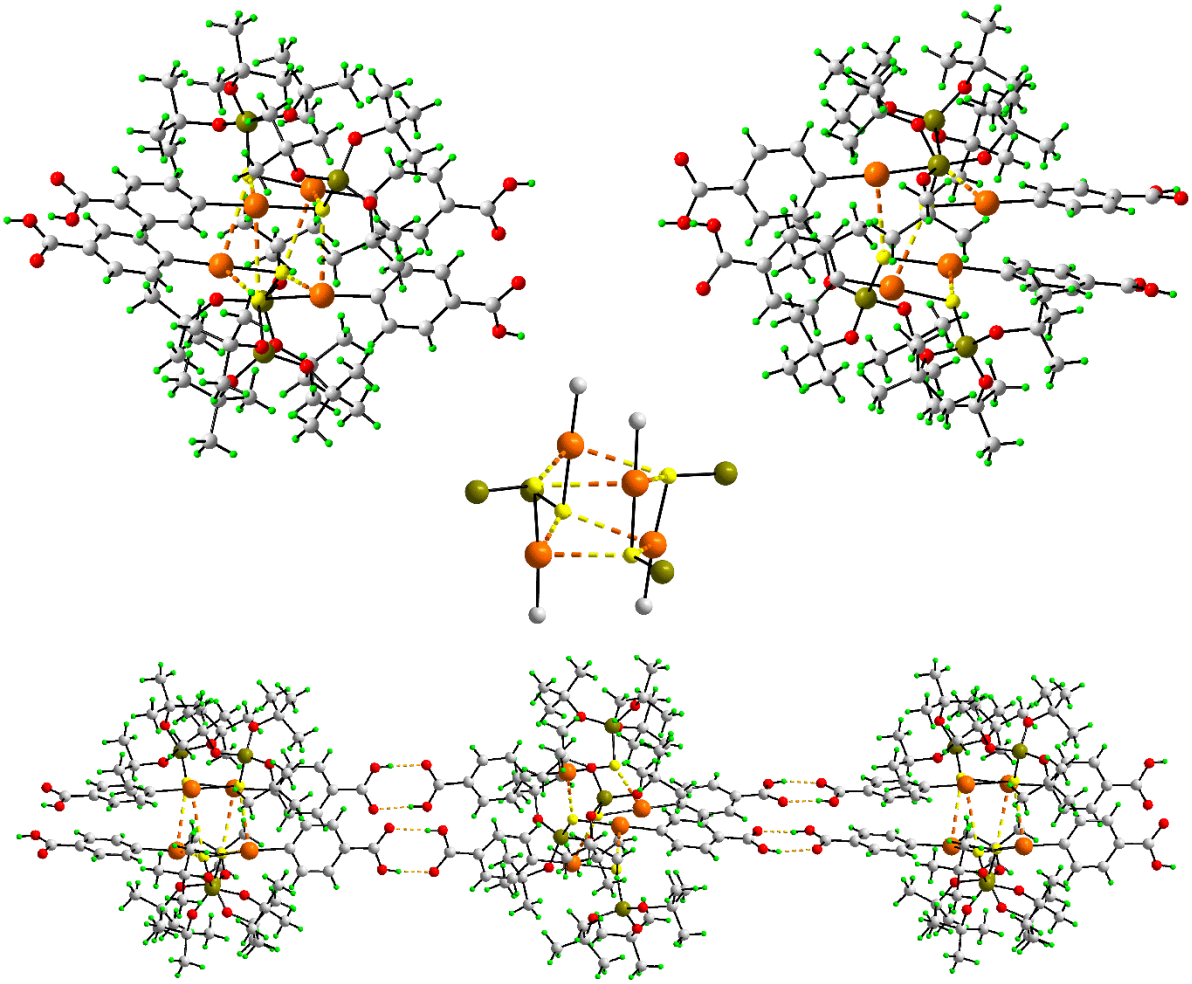

Figure S36. XUYROY 4-(Tri-t-butoxysilylthiomercurio)benzoic acid [67].

d(Hg···S) = 3.2465(15) Å; Hg–S···Hg = 95.0(4)°; Si–S···Hg = 138.66(7)°

S–Hg···S = 88.83(4)°; C–Hg···S = 97.33(13)°

d(Hg···S) = 3.3737(15) Å; Hg–S···Hg = 92.27(4)°; Si–S···Hg = 138.23(8)°

S–Hg···S = 83.92(4)°; C–Hg···S = 96.46(13)°

d(Hg···S) = 3.2365(18) Å; Hg–S···Hg = 104.34(6)°; Si–S···Hg = 151.10(9)°

S–Hg···S = 87.11(5)°; C–Hg···S = 95.54(18)°

{Two independent molecules. Each assembles into a tetrameric aggregate about a four-fold inversion centre (entry 1). For the first molecule, a distorted cube arises if one considers an interaction a little longer than the search criteria (second entry)}; the second tier Hg···S separations for the second tetramer to form the cube are considerably longer at 3.7255(16) Å. The tetrameric molecules assemble into a helical (4_1-screw symmetry) supramolecular chain via carboxylate-O–H···O(carbonyl) hydrogen bonds}

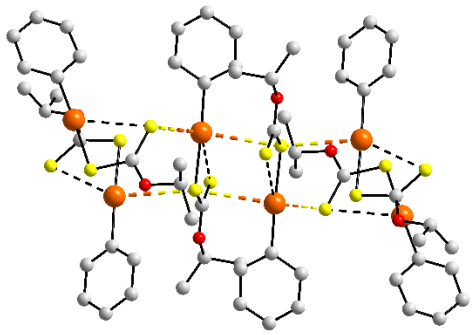

Figure S37. FOKBEM Phenyl-(isopropylxanthate-S)mercury(II) [65].

d(Hg···S) = 3.306(5) Å; Hg–S···Hg = 95.03(13)°; C–S···Hg = 86.3(5)°

S–Hg···S = 84.97(12)°; C–Hg···S = 97.0(3)°

d(Hg···S) = 3.332(4) Å; Hg–S···Hg = 97.51(13)°; C–S···Hg = 86.1(5)°

S–Hg···S = 85.19(9)°; C–Hg···S = 93.4(4)°

d(Hg···S) = 3.329(4) Å; C–S···Hg = 118.3(5)°

S–Hg···S = 80.91(13)°; C–Hg···S = 94.7(4)°

{There are three independent molecules in the asymmetric unit. One pair associates about a centre of inversion and a $\{\cdots Hg–S\}_2$ synthon (Hg···S = 3.306(5) Å). Each mercury atom of the dimer accepts a second Hg···S interaction (3.332(4) Å) from a pair of second independent molecules with the potential to form a second $\{\cdots Hg–S\}_2$ synthon but the second Hg···S separation well exceeds the sum of the van der Waals radii (3.457(3) Å). At the same time employs the mercury atoms to form a pair of Hg···S contacts (3.3286(4) Å) with the third independent molecules. The result is a six-molecule aggregate. Intramolecular Hg···S interactions are also noted, being 3.159(5), 3.309(4) & 3.211(4) Å}

2. One-dimensional aggregation patterns sustained by Hg···S secondary-bonding interactions.

2.1. Linear

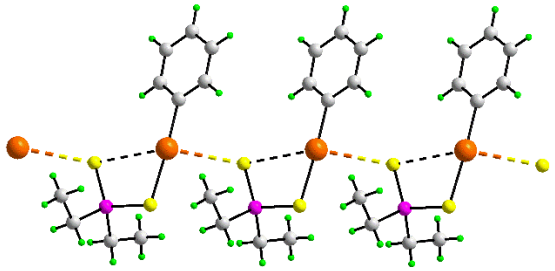

Figure S38. LENZIN (Diethyldithiophosphinato-S)-phenyl-mercury(II) [69].

d(Hg···S) = 3.182(3) Å; P–S···Hg = 119.32(2)°

S–Hg···S = 91.12(7)°; C–Hg···S = 91.9(4)°

{Molecules assemble into a linear, one-dimensional chain via Hg···S contacts. An intramolecular Hg···S contact is also noted: 3.182(3) Å}

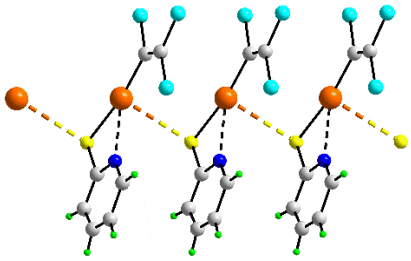

Figure S39. QIQHIH (2-Pyridylthiolato)-trichlorovinyl-mercury(II) [70].

d(Hg···S) = 3.330(7) Å; Hg–S···Hg = 89.1(2)°; C–S···Hg = 108.4(8)°

S–Hg···S = 89.1(2)°; C–Hg···S = 98.5(7)°

{Molecules assemble into a linear, one-dimensional chain via Hg···S contacts. An intramolecular Hg···N contact is also noted: 2.808(19) Å}

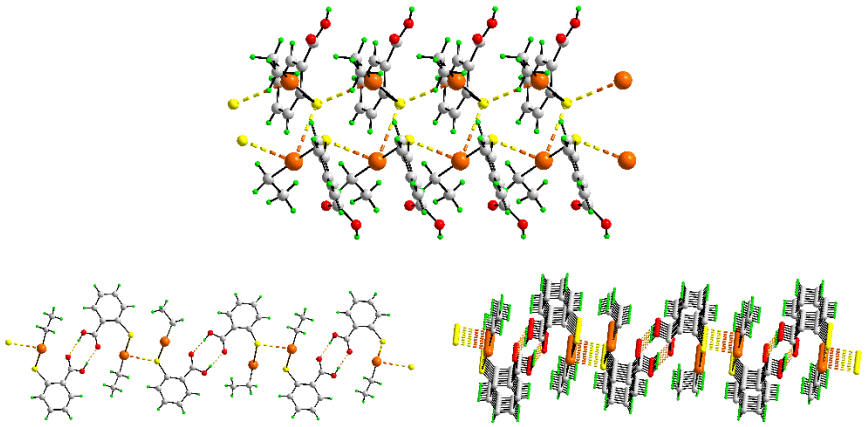

Figure S40. XUHREY Ethyl-(2-carboxybenzenethiolato)-mercury(II) [71].

d(Hg···S) = 3.2613(13) Å; Hg–S···Hg = 90.14(4)°; C–S···Hg = 112.99(17)°

S–Hg···S = 90.14(4)°; C–Hg···S = 94.48(14)°

d(Hg···S) = 3.3247(13) Å; Hg–S···Hg = 90.72(4)°; C–S···Hg = 128.08(17)°

S–Hg···S = 90.72(4)°; C–Hg···S = 99.09(16)°

d(Hg···S) = 3.2851(13) Å; Hg–S···Hg = 85.13(4)°; C–S···Hg = 117.01(17)°

S–Hg···S = 71.15(4)°; C–Hg···S = 104.42(14)°

d(Hg···S) = 3.2252(13) Å; Hg–S···Hg = 91.03(4)°; C–S···Hg = 124.98(17)°

S–Hg···S = 91.03(4)°; C–Hg···S = 93.63(14)°

d(Hg···S) = 3.3110(13) Å; Hg–S···Hg = 89.10(4)°; C–S···Hg = 142.93(17)°

S–Hg···S = 89.10(4)°; C–Hg···S = 98.46(14)°

d(Hg···S) = 3.3567(13) Å; Hg–S···Hg = 80.43(4)°; C–S···Hg = 108.57(16)°

S–Hg···S = 72.19(4)°; C–Hg···S = 106.37(15)°

{There are four independent molecules in the asymmetric unit and each of these assemble into a linear, one-dimensional chain via an average of one Hg···S contact per molecule; entries 1, 2, 4 and 5. Two of the strands (entries 1 and 2) are connected into a supramolecular tape via a further Hg···S contact (entry 3). If an additional Hg···S contact is taken into account, which is just beyond the sum of the van der Waals radii, i.e., Hg···S = 3.3567(13) Å, entry 6, the other two strands (entries 4 and 5) are also connected into a tape. The tapes are connected into a supramolecular layer via carboxylate-O–H···O(carbonyl) hydrogen bonds. Finally, each mercury atom forms and intramolecular Hg···O(carbonyl) interaction with separations in the range from 2.872(4) to 2.901(4) Å. See XUHREY01 (**47**), a polymorph}

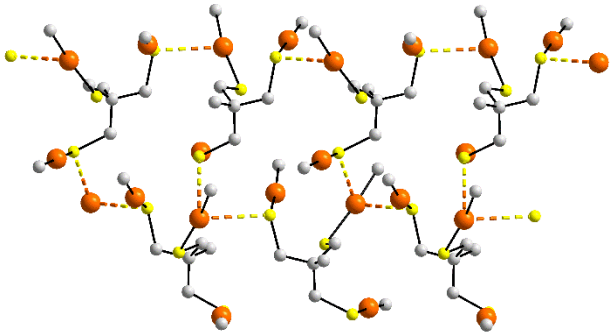

Figure S41. WAYPAN Trimethyl-(μ_3-1,1,1-tris(mercaptomethyl)ethane-S,S',S'')-tri-mercury(II) [72].

d(Hg···S) = 3.212(6) Å; Hg–S···Hg = 112.6(2)°; C–S···Hg = 100.8(7)°

S–Hg···S = 98.12(19)°; C–Hg···S = 93.1(7)°

d(Hg···S) = 3.344(7) Å; Hg–S···Hg = 116.4(2)°; C–S···Hg = 104.1(8)°

S–Hg···S = 98.0(2)°; C–Hg···S = 91.6(8)°

d(Hg···S) = 3.311(7) Å; Hg–S···Hg = 129.4(2)°; C–S···Hg = 100.5(8)°

S–Hg···S = 97.9(2)°; C–Hg···S = 87.0(8)°

{There are two independent tri-nuclear molecules and each of these assemble into a zig-zag, one-dimensional chain via an average of one Hg···S contact per molecule. Adjacent chains assemble via a further inter-chain Hg···S contact (third entry) to form a linear, double chain}

2.2. Zigzag

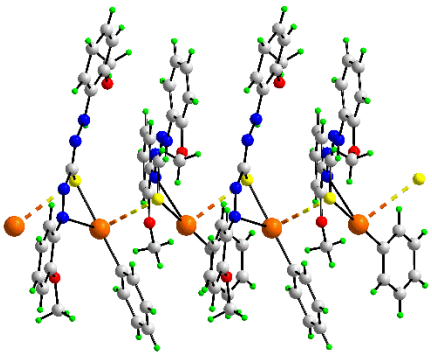

Figure S42. OBIZAC (1,5-bis(2-Methoxyphenyl)thiocarbazonato)-phenyl-mercury(II) [73].

d(Hg···S) = 3.2929(10) Å; Hg–S···Hg = 81.11(3)°; C–S···Hg = 100.79(14)°

S–Hg···S = 93.96(3)°; C–Hg···S = 86.43(11)°

{The molecules associate into a zig-zag supramolecular chain propagated by glide symmetry. An intramolecular Hg···N contact of 2.725(3) Å is noted}

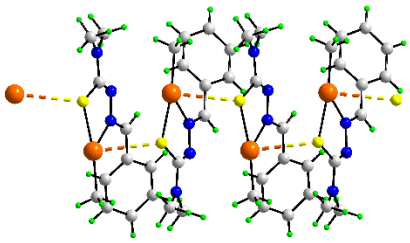

Figure S43. NESRUA (N'-Benzylidene-N,N-dimethylcarbamohydrazonothioato)-(methyl)mercury(II) [74].

d(Hg···S) = 3.293(5) Å; Hg–S···Hg = 102.31(17)°; C–S···Hg = 97.5(5)°

S–Hg···S = 90.48(16)°; C–Hg···S = 92.5(6)°

{The molecules assemble into a zigzag, one-dimensional chain via Hg···S contacts. Intramolecular Hg···N contacts of 2.603(16) Å are noted}

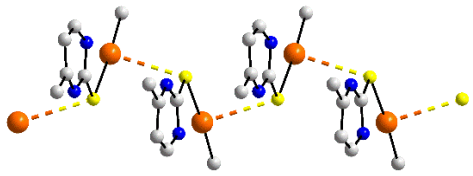

Figure S44. DOYFIG Methyl-(2-mercapto-4-methylpyrimidinato)-mercury(II) [75].

d(Hg···S) = 3.325(11) Å; Hg–S···Hg = 117.9(3)°; C–S···Hg = 89.3(8)°

S–Hg···S = 91.6(3)°; C–Hg···S = 92(1)°

{The molecules associate into a zig-zag supramolecular chain propagated by glide symmetry. An intramolecular Hg···N contact of 3.02(6) Å is noted as are Hg···Hg contacts [3.805(3) Å] leading to double chains}

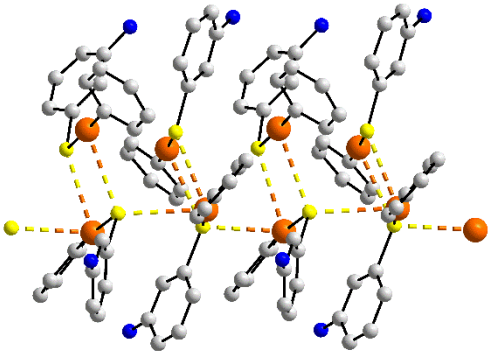

Figure S45. QUGVIX (3-Aminophenylthiolato)-phenyl-mercury(II) [66].

d(Hg···S) = 3.184(7) Å; Hg–S···Hg = 96.29(12)°; C–S···Hg = 140.2(6)°

S–Hg···S = 85.23(16)°; C–Hg···S = 97.4(7)°

d(Hg···S) = 3.251(7) Å; Hg–S···Hg = 94.59(12)°; C–S···Hg = 132.7(7)°

S–Hg···S = 83.69(16)°; C–Hg···S = 97.8(7)°

d(Hg···S) = 3.229(5) Å; Hg–S···Hg = 109.91(8)°; C–S···Hg = 107.8(7)°

S–Hg···S = 89.87(13)°; C–Hg···S = 95.0(5)°

{Two independent molecules assemble into a dimeric aggregate via two Hg···S interactions (first two entries). These associate into a zig-zag supramolecular chain propagated by glide symmetry}

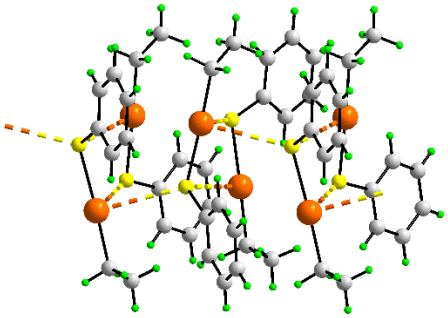

Figure S46. DOFNOC Ethyl-(phenylthiolato)-mercury(II) [76].

d(Hg···S) = 3.226(2) Å; Hg–S···Hg = 96.60(7)°; C–S···Hg = 108.6(3)°

S–Hg···S = 81.75(8)°; C–Hg···S = 96.4(3)°

d(Hg···S) = 3.312(2) Å; Hg–S···Hg = 94.79(7)°; C–S···Hg = 145.0(3)°

S–Hg···S = 79.58(7)°; C–Hg···S = 101.9(3)°

d(Hg···S) = 3.272(2) Å; Hg–S···Hg = 119.07(8)°; C–S···Hg = 108.5(3)°

S–Hg···S = 89.53(7)°; C–Hg···S = 92.6(3)°

{Two independent molecules assemble into a dimeric aggregate via two Hg···S interactions (first two entries). These associate into a zig-zag supramolecular chain propagated by glide symmetry}

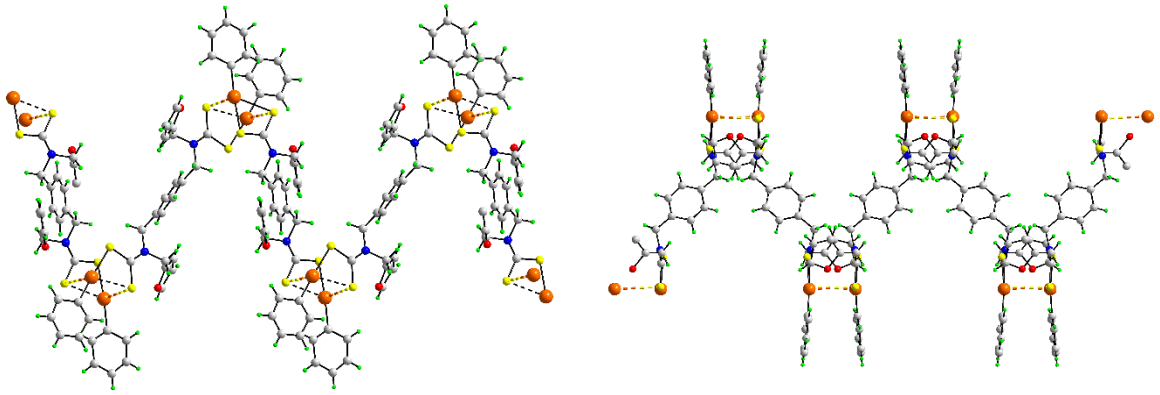

Figure S47. YOMXIJ ((μ2-(2-furylmethyl)(4-(((2-furylmethyl)((sulfanyl)(thioxo)methyl)amino)methyl)-benzyl)carbamodithioato)-diphenyl-di-mercury [50].

d(Hg···S) = 3.254(5) Å; Hg–S···Hg = 85.66(13)°; C–S···Hg = 92.7(5)°

S–Hg···S = 93.07(16)°; C–Hg···S = 94.7(5)°

{The di-nuclear molecule is disposed about a centre of inversion. Each end associate about a 2-fold axis of symmetry to form a zig-zag supramolecular chain propagated by glide symmetry. An intramolecular Hg···S interaction of 2.933(8) Å is noted}

2.3. Helical

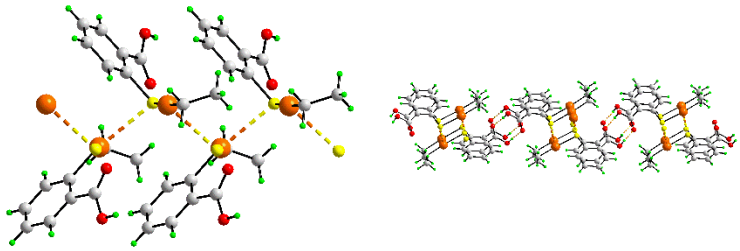

Figure S48. XUHREY01 Ethyl-(2-carboxybenzenethiolato)-mercury(II) [71].

d(Hg···S) = 3.0809(10) Å; Hg–S···Hg = 109.03(4)°; C–S···Hg = 87.97(13)°

S–Hg···S = 85.62(3)°; C–Hg···S = 94.35(13)°

{The molecules assemble into a helical (2_1-screw symmetry), one-dimensional chain via an average of one Hg···S contact per molecule. The tapes are connected into a supramolecular layer via carboxylate-O–H···O(carbonyl) hydrogen bonds. An intramolecular Hg···O(carbonyl) interaction is absent as the carbonyl-oxygen atom is directed away from the mercury atom. See XUHREY (**40**), for a polymorph}

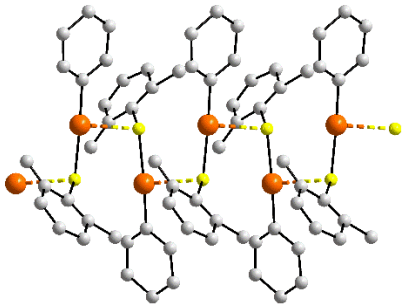

Figure S49. PHGMSP Phenylmercury-(2,6-dimethyl-thiophenolate) [77].

d(Hg···S) = 3.183(15) Å; Hg–S···Hg = 102.1(4)°; C–S···Hg = 114(1)°

S–Hg···S = 86.4(4)°; C–Hg···S = 100(2)°

{The molecules assemble into a helical (2_1-screw symmetry), one-dimensional chain via Hg···S contacts}

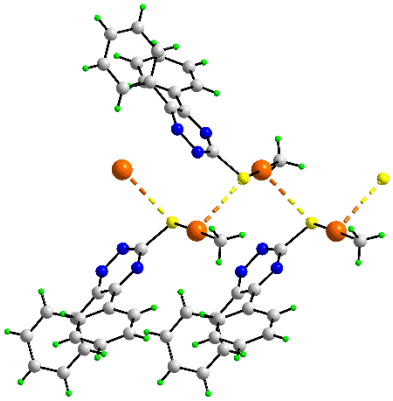

Figure 50. OCOLEY (4,5-Diphenyl-(1,2,4)triazine-3-thionato)-methyl-mercury [78].

d(Hg···S) = 3.3251(17) Å; Hg–S···Hg = 133.46(6)°; C–S···Hg = 87.6(2)°

S–Hg···S = 78.08(5)°; C–Hg···S = 101.2(2)°

{The molecules assemble into a helical (2_1-screw symmetry) one-dimensional chain via Hg···S contacts. Intramolecular Hg···N contacts of 3.146(5) Å are noted}

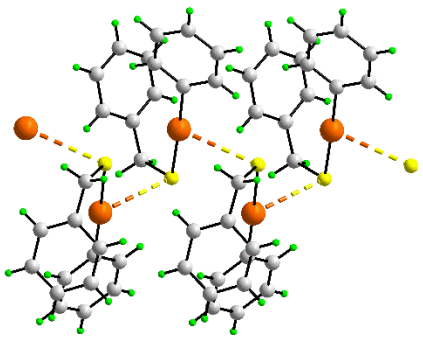

Figure S51. LAWTUB Phenyl(phenylmethanethiolato)mercury(II) [79].

d(Hg···S) = 3.290(3) Å; Hg–S···Hg = 95.82(7)°; C–S···Hg = 88.6(3)°

S–Hg···S = 86.23(7)°; C–Hg···S = 95.7(3)°

{Molecules assemble into a helical chain (2_1-screw symmetry) down the c-axis}

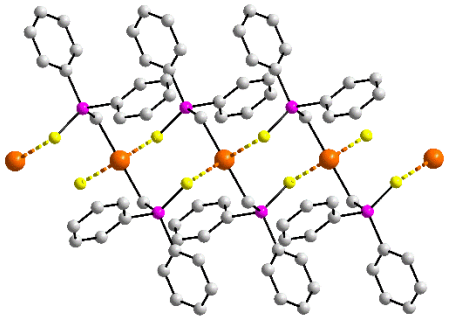

Figure S52. GILNOE bis(Methylene(diphenyl)thiophosphinate)-mercury(II) [80].

d(Hg···S) = 2 × 3.179(5) Å; P–S···Hg = 103.6(2)°

C–Hg···S = 89.0(5) & 91.6(5)°

{Molecules have 2-fold symmetry and assemble into a helical, one-dimensional chain via an average of two Hg···S contacts per molecule and eight-membered $\{\cdots HgCPS\}_2$ synthons with chair conformations whereby one each of the P–C bonds lies above and below the plane defined by the $\{HgS\}_2$ atoms}

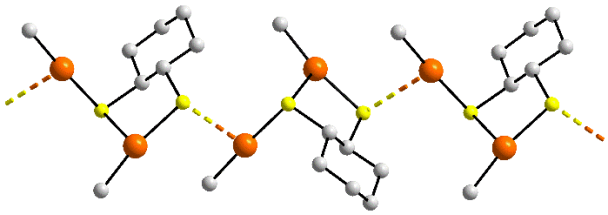

Figure S53. CHMEHG (μ-trans-Cyclohexane-1,2-dithiolato)-bis(methyl-mercury(II)) 1980 [81].

d(Hg···S) = 3.296(4) Å; Hg–S···Hg = 105.28(13)°; C–S···Hg = 104.2(4)°

S–Hg···S = 86.56(15)°; C–Hg···S = 96.5(7)°

{Di-nuclear molecules assemble into a helical, one-dimensional chain via a single Hg···S contact; an intramolecular Hg···S contact of 2.853(16) Å is noted}

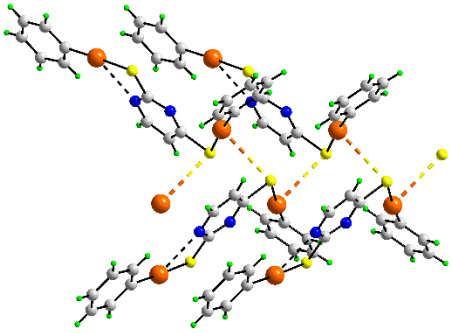

Figure S54. LOPGUT (μ_2-2,4-Pyrimidinedithiolato)-diphenyl-di-mercury(II) [82].

d(Hg···S) = 3.303(4) Å; Hg–S···Hg = 114.98(12)°; C–S···Hg = 83.6(4)°

S–Hg···S = 79.66(11)°; C–Hg···S = 95.7(4)°

{The di-nuclear molecules into a helical, one-dimensional chain via Hg···S contacts involving one mercury atom only. Weaker, intra-chain Hg···S contacts of 3.369(4) Å involving the same mercury atom and the second sulphur atom are noted. An intramolecular Hg···N contact of 2.774(11) Å is also noted}

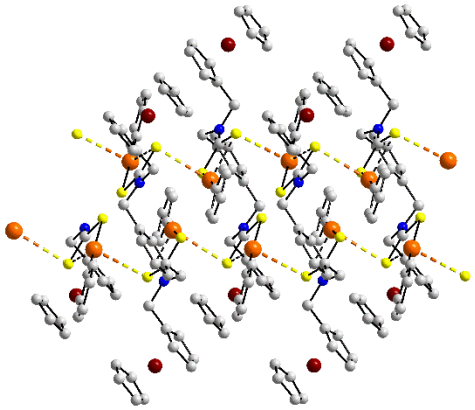

Figure S55. FUPFOM (μ2-N,N'-(1,3-dimethylphenylene)-bis(ferrocenylmethyldithiocarbamato))-bis(phenyl-mercury) diethyl ether solvate [40].

d(Hg···S) = 3.268(3) Å; C–S···Hg = 91.1(4)°

S–Hg···S = 83.52(9)°; C–Hg···S = 96.6(3)°

d(Hg···S) = 3.303(3) Å; C–S···Hg = 91.7(4)°

S–Hg···S = 84.37(9)°; C–Hg···S = 95.4(3)°

{The non-symmetric di-nuclear molecule associates into a helical supramolecular chain via two Hg···S interactions, one per mercury atom. The dithiocarbamate ligands link the chains into a tape. An intramolecular Hg···S contact in each residue is noted = 2.877(3) and 2.882(3) Å}

2.4. Twisted

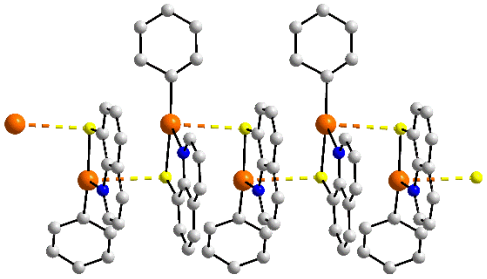

Figure S56. CECWOW 8-Mercaptoquinolinato-phenyl-mercury(II) [83].

d(Hg···S) = 3.249(11) Å; Hg–S···Hg = 93.99(18)°; C–S···Hg = 100.7(3)°

S–Hg···S = 89.40(18)°; C–Hg···S = 92.1(7)°

d(Hg···S) = 3.350(6) Å; Hg–S···Hg = 95.6(2)°; C–S···Hg = 102.3(2)°

S–Hg···S = 87.74(18)°; C–Hg···S = 94.0(7)°

{Two independent molecules. These are connected by the shortest Hg···S contact. The dimers assemble into a twisted, one-dimensional chain owing to the skewed disposition of the independent molecules. Two additional intra-chain Hg···S contacts are noted, i.e., 3.349(11) and 3.395(6) Å which when combined with the above generates a supramolecular tape. Intramolecular Hg···N contacts are also present: 2.46(2) and 2.46(2) Å}

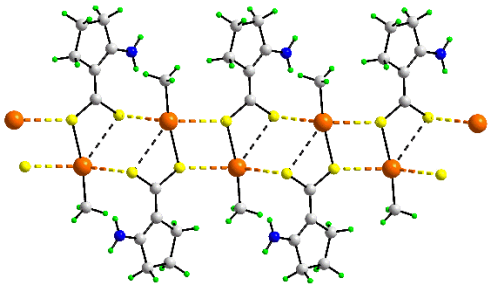

Figure S57. IHOLEW01 (2-Aminocyclopent-1-ene-1-carbodithioato)-methyl-mercury(II) [39].

d(Hg···S) = 3.1797(17) Å; C–S···Hg = 94.64(15)°

S–Hg···S = 90.45(4)°; C–Hg···S = 96.72(17)°

d(Hg···S) = 3.3501(12) Å; Hg–S···Hg = 111.66(4)°; C–S···Hg = 145.95(16)°

S–Hg···S = 68.34(4)°; C–Hg···S = 105.81(17)°

{Two molecules associated about a centre of inversion to form a dimer, involving the shorter of the Hg···S contacts. The dimers are connected into a linear, supramolecular chain by Hg···S at the limit of the search criteria. An intramolecular Hg···S contact is noted with Hg···S = 3.1747(11) Å. See IHOLEW (**1**) for a polymorphic crystal}

2.5. Square-Wave

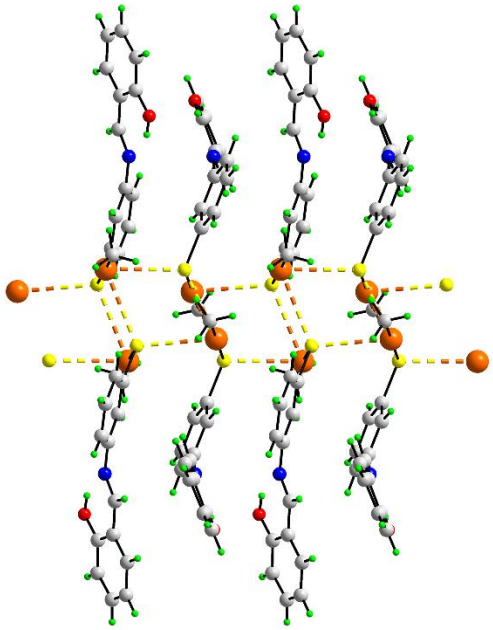

Figure S58. QUGVOD (3-(o-Hydroxybenzylideneamino)phenylthiolato)-methyl-mercury(II) [66].

d(Hg···S) = 3.240(3) Å; Hg–S···Hg = 95.18(10)°; C–S···Hg = 131.4(4)°

S–Hg···S = 84.82(10)°; C–Hg···S = 96.3(5)°

d(Hg···S) = 3.251(3) Å; Hg–S···Hg = 91.80(11)°; C–S···Hg = 131.3(4)°

S–Hg···S = 88.20(11)°; C–Hg···S = 93.5(4)°

d(Hg···S) = 3.128(3) Å; Hg–S···Hg = 106.76(11)°; C–S···Hg = 111.9(4)°

S–Hg···S = 88.27(10)°; C–Hg···S = 92.8(5)°

d(Hg···S) = 3.160(3) Å; Hg–S···Hg = 108.01(11)°; C–S···Hg = 107.3(4)°

S–Hg···S = 87.11(10)°; C–Hg···S = 93.1(4)°

{Two independent molecules and each assembles into a dimeric aggregate across an inversion centre of via two Hg···S interactions (first two entries). These associate into a supramolecular chain (square-wave) owing to the different orientations of the dimeric aggregates}

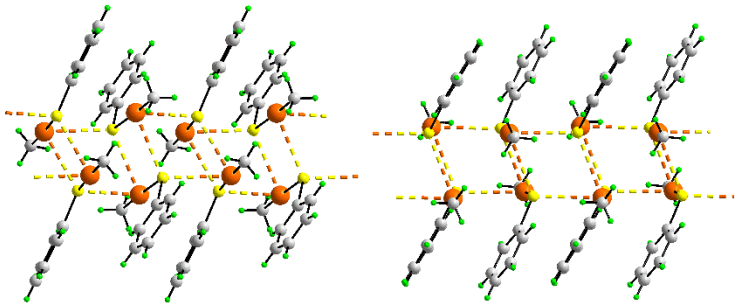

Figure S59. DOFNIW Methyl-(phenylthiolato)-mercury(II) [76].

d(Hg···S) = 3.2491(14) Å; Hg–S···Hg = 96.07(5)°; C–S···Hg = 127.22(17)°

S–Hg···S = 83.93(4)°; C–Hg···S = 97.3(2)°

d(Hg···S) = 3.2406(13) Å; Hg–S···Hg = 104.36(5)°; C–S···Hg = 109.2(2)°

S–Hg···S = 88.65(4)°; C–Hg···S = 94.80(19)°

{Molecules assemble about a centre of inversion, Hg···S = 3.2491(14) Å, to form a $\{HgS\cdots\}_2$ rectangle. These are related to neighbouring rectangles via 2-fold symmetry with the result a supramolecular chain with a square-wave topology eventuates}

3. Two-dimensional array sustained by Hg···S secondary-bonding interactions

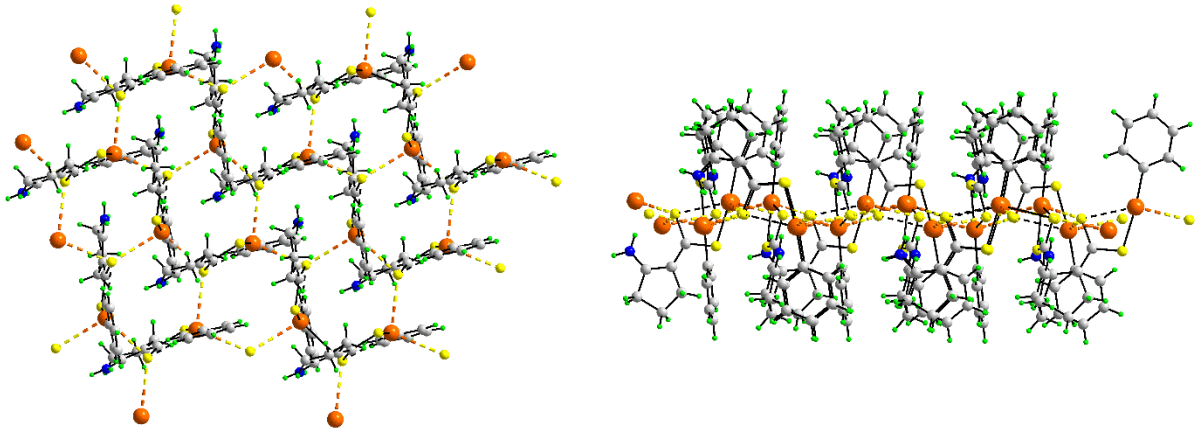

Figure S60. IHOLIA (2-Aminocyclopent-1-ene-1-carbodithioato)-phenyl-mercury(II) [39].

d(Hg···S) = 3.1834(11) Å; C–S···Hg = 98.61(13)°

S–Hg···S = 93.66(3)°; C–Hg···S = 90.88(12)°

d(Hg···S) = 3.2269(10) Å; C–S···Hg = 102.17(12)°

S–Hg···S = 81.60(3)°; C–Hg···S = 101.38(10)°

{The mercury atom forms two Hg···S contacts with two different molecules so a hexagonal arrangement of Hg···S contacts is apparent when two intramolecular contacts are taken into account. The noted intramolecular Hg···S contact has Hg···S = 3.1286(10) Å}

4. Aggregation patterns sustained by Hg···S secondary-bonding interactions in supramolecular coordination polymers

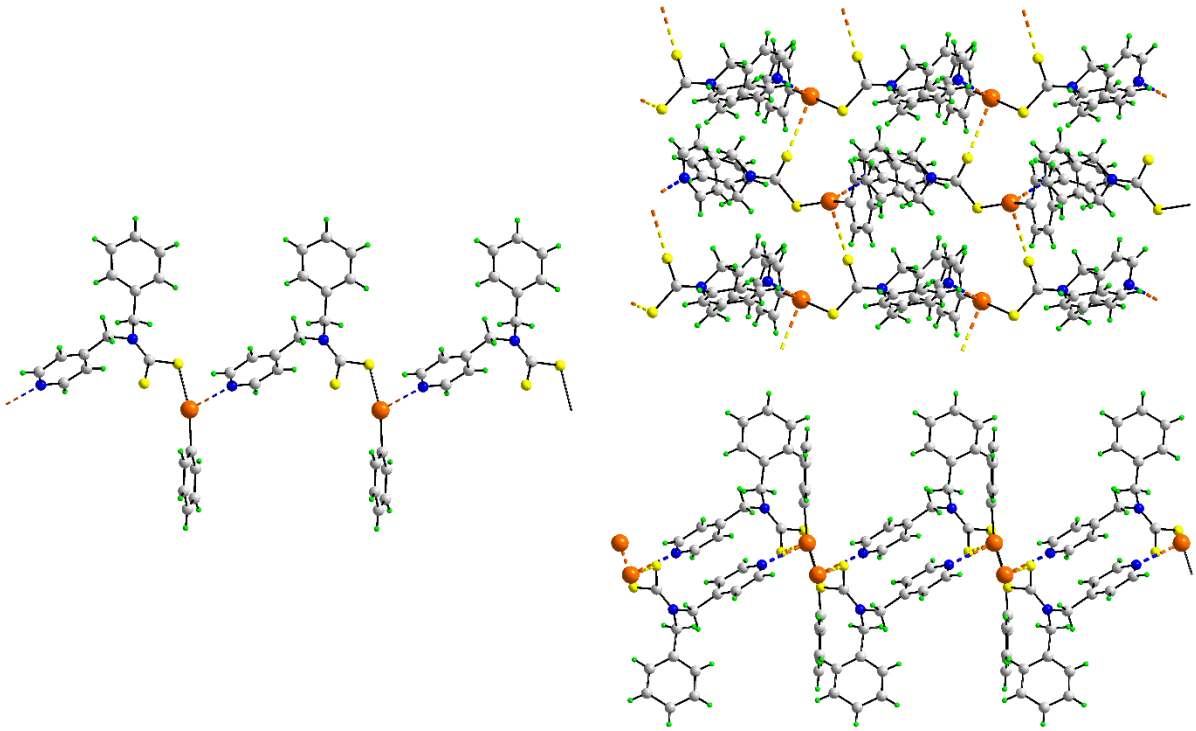

Figure S61. EBUSIF Phenyl-(benzyl(pyridin-4-ylmethyl)carbamodithioato)-mercury(II) [86].

d(Hg···S) = 3.203(5) Å; C–S···Hg = 122.7(7)°

S–Hg···S = 79.0(2)°; C–Hg···S = 100.5(5)°

{Molecules assemble into a linear (translational symmetry) coordination polymer as the multi-functional dithiocarbamate ligand is bidentate, bridging via one sulphur and a pyridyl-nitrogen atom (Hg···N = 2.74(2) Å); an intramolecular Hg···S contact (= 2.993(5) Å) is noted. Chains are connected into a two-dimensional array with a step-ladder topology via Hg···S interactions}

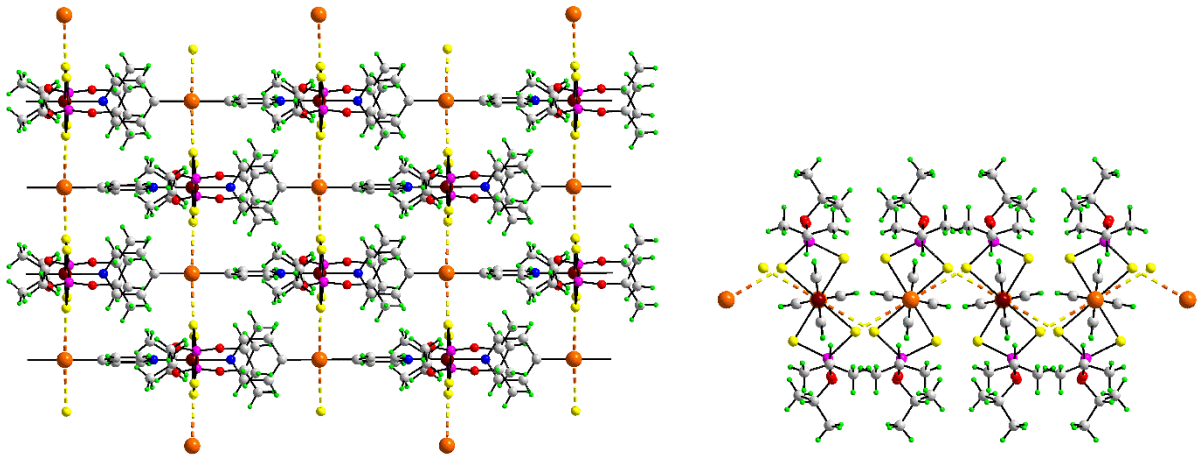

Figure S62. COCJUC catena-(bis(μ-Pyridin-4-yl)-bis(O,O'-di-isopropyldithiophosphato)-mercury-nickel(II) [87].

d(Hg···S) = 3.2960(12) Å; Ni–S···Hg = 109.33(4)°; P–S···Hg = 165.54(7)°

C–Hg···S = 88.58(17) & 91.42(17)°; S···Hg···S = 177.17(3)°

{Di(4-pyridyl)mercury molecules link $Ni[S_2P(O\text{-}i\text{-}Pr)_2]_2$ molecules into a linear supramolecular chain situated about a 2-fold axis of symmetry. The chains are assembled into a flat, two-dimensional array by Hg···S interactions}