The remarkable propensity for the formation of C–H···π(chelate ring) interactions in the crystals of the first-row transition metal dithiocarbamates and the supramolecular architectures they sustain

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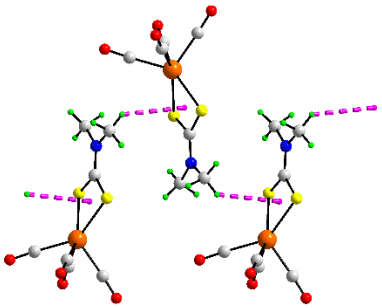
Electronic Supplementary Information

Images of supramolecular association with geometric details mediated by C–H···π(chelate ring) interactions in the crystals of titanium (**1**), vanadium (**2**-**8**), chromium (**9**-**13**), manganese (**14**), iron (**15**-**33**), cobalt (**34**-**39**), nickel (**40**-**126**) and copper (**127**-**166**) dithiocarbamate complexes. Non-participating species, such as solvent, counterions, *etc*. are not illustrated herein.

TITANIUM



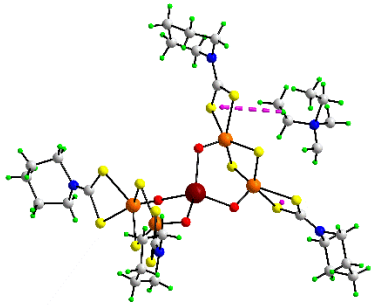
1. ODONAX: *catena*-[bis(μ2-Carbonyl)-dicarbonyl-(18-crown-6)-(dimethyldithiocarbamato)-potassium-titanium(0)]

R. E. Jilek, G. Tripepi, E. Urnezius, W. W. Brennessel, V. G. Young Jr and J. E. Ellis, *Chem. Commun*. 2007, pp. 2639-2641; doi: 10.1039/B700808B

d = 3.00 Å, C–H···Cg(chelate ring) = 137° and θ = 11°

{Each dithiocarbamate ligand accepts a N-methyl-C–H···Cg(chelate ring) interaction to form a helical (2_1) supramolecular chain; unusual trigonal-prismatic coordination geometry for Ti(0)}

VANADIUM

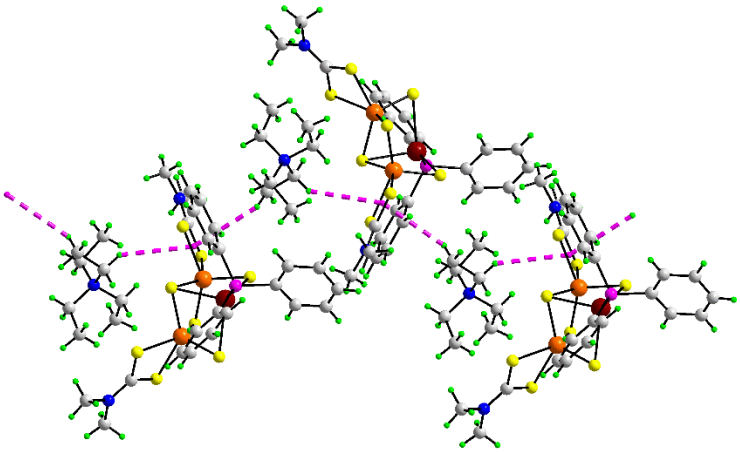


2. MIBXOK: bis(Tetraethylammonium) ammonium tetrakis(μ2-oxo)-tetrakis(μ2-sulfido)-tetrakis(pentamethylenedithiocarbamato)-sodium-tetra-vanadium

H. Zhu, C. Chen, X. Zhang, Q. Liu, D. Liao and L. Li, *Inorg. Chim. Acta*, 2002, **328**, 96-104; doi: 10.1016/S0020-1693(01)00714-9

d = 3.29 Å, C–H···Cg(chelate ring) = 121° and θ = 13°

{A dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction from an ammonium cation to form a zero-dimensional aggregate}



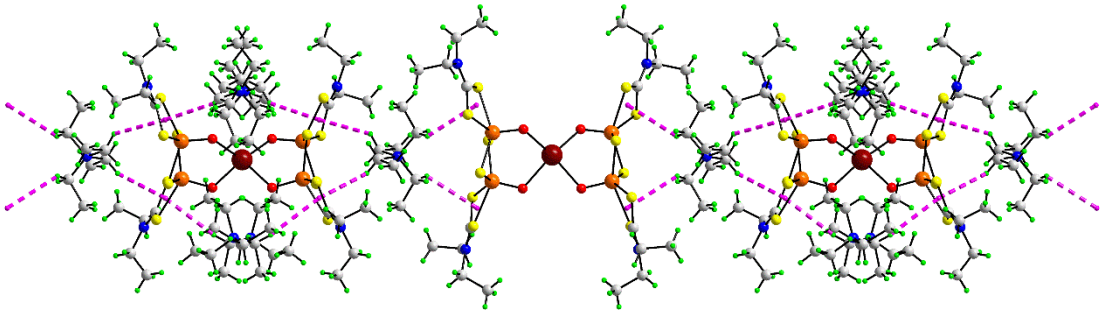
3. SAQDAP: Tetraethylammonium (μ_3-sulfido)-tris(μ_2-sulfido)-bis(dimethyldithiocarbamato)-triphenylphosphino-silver-di-vanadium(IV) acetonitrile solvate

H. Zhu, Q. Liu, X. Huang, T. Wen, C. Chen and D. Wu, *Inorg. Chem.*, 1998, **37**, 2678-2686; doi: 10.1021/ic9715310

d = 3.27 Å, C–H···Cg(chelate ring) = 144° and θ = 19°

d = 3.27 Å, C–H···Cg(chelate ring) = 133° and θ = 12°

{A dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) and a methyl-C–H···Cg(chelate ring) interaction from two symmetry related ammonium cations to form a helical (2_1) supramolecular chain}



4. SAQDIX: tris(Tetraethylammonium) sodium bis(bis(μ_2-sulfido)-bis[(diethyldithiocarbamatooxo-vanadium)] methanol solvate hemihydrate

H. Zhu, Q. Liu, X. Huang, T. Wen, C. Chen and D. Wu, *Inorg. Chem.*, 1998, **37**, 2678-2686; doi: 10.1021/ic9715310

d = 2.98 Å, C–H···Cg(chelate ring) = 120° and θ = 17°

d = 3.05 Å, C–H···Cg(chelate ring) = 119° and θ = 14°

d = 2.93 Å, C–H···Cg(chelate ring) = 126° and θ = 9°

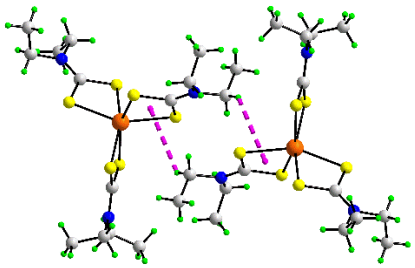
d = 3.01 Å, C–H···Cg(chelate ring) = 137° and θ = 13°

d = 2.84 Å, C–H···Cg(chelate ring) = 139° and θ = 6°

d = 3.10 Å, C–H···Cg(chelate ring) = 159° and θ = 12°

{There are two independent 2-fold symmetric sodium tetra-vanadium aggregates in the asymmetric unit. These differ in their mode of association with the ammonium cations through N-methylene-C–H···Cg(chelate ring) interactions. For the central aggregate in the figure, each dithiocarbamate ligand

accepts a single N-methylene-C–H···Cg(chelate ring) interaction provided by two methylene groups of a single ammonium cation; first two entries. This same cation, *via* the two remaining methylene groups bridges two second independent aggregates *via* N-methylene-C–H···Cg(chelate ring) interactions; entries three and four. Each dithiocarbamate ligands for this second independent molecule also accepts a second N-methylene-C–H···Cg(chelate ring) contact from a terminally bound ammonium cation, entries five and six. The result is a supramolecular chain with a twisted topology}

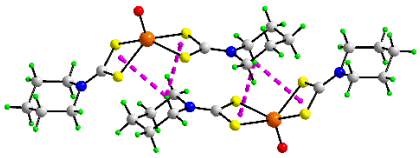


5. RAVHAX: tris(Diethyldithiocarbamato)vanadium(III)

H.-P. Zhu, Y.-H. Deng, X.-Y. Huang, C.-N. Chen and Q.-T. Liu, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., 1997, **53**, 692-693; doi: 10.1107/S0108270196015065

d = 3.27 Å, C–H···Cg(chelate ring) = 126° and θ = 19°

{Centrosymmetrically related molecules self-assemble to form a dimeric aggregate *via* a pair of N-methylene-C–H···Cg(chelate ring) interactions}



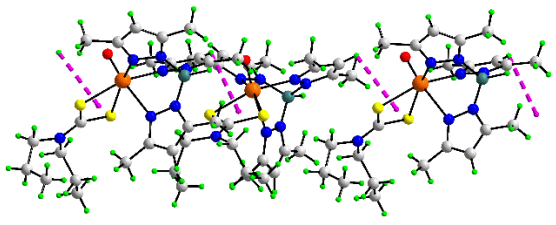
6. QIZXIJ: Oxido-bis(piperidine-1-carbodithioato)vanadium(IV)

A. Machálková, I. Charamzová, J. Honzíček, J. Vinklárek and I. Cisařová, *Z. Kristallogr.-New Cryst. Struct*., 2019, **234**, 223-225; doi: 10.1515/ncrs-2018-0265

d = 2.92 Å, C–H···Cg(chelate ring) = 146° and θ = 5°

d = 3.04 Å, C–H···Cg(chelate ring) = 152° and θ = 12°

{A methylene-hydrogen is bifurcated, forming two N-methylene-C–H···Cg(chelate ring) interactions, thereby linking two dithiocarbamate ligands in a centrosymmetric aggregate}

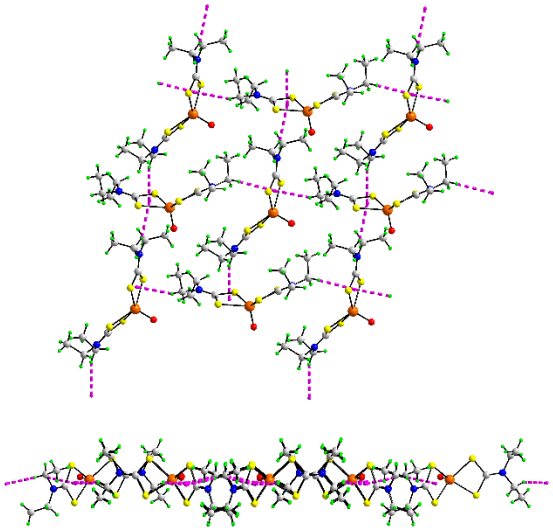


7. JETMAW: (Dipropyldithiocarbamato)-(tris(3,5-dimethyl-1-pyrazolyl)-hydroborato)-oxo-vanadium(IV)

N. E. Heimer and W. E. Cleland Jr, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., 1990, **46**, 2049-2051; doi: 10.1107/S0108270190001512

d = 3.28 Å, C–H···Cg(chelate ring) = 105° and θ = 12°

{A dithiocarbamate ligand accepts a pyrazolyl-C–H···Cg(chelate ring) interaction to form a zig-zag (glide symmetry) supramolecular chain}



8. ETCOXV01: bis(Diethylcarbamodithioato)-oxido-vanadium(IV)

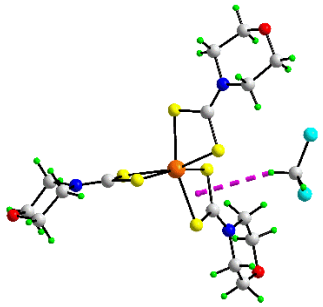
M. Atzori, L. Tesi, S. Benci, A. Lunghi, R. Righini, A. Taschin, R. Torre, L. Sorace and R.Sessoli, *J. Am. Chem. Soc*., 2017, **139**, 4338-4341; doi: 10.1021/jacs.7b01266

d = 2.74 Å, C–H···Cg(chelate ring) = 153° and θ = 9°

d = 2.88 Å, C–H···Cg(chelate ring) = 156° and θ = 7°

{A dithiocarbamate ligand accepts a two N-methylene-C–H···Cg(chelate ring) interactions to form a 2-D grid with an undulating topology}

CHROMIUM

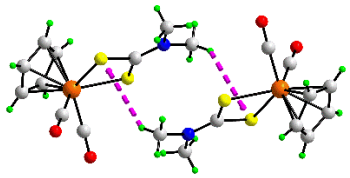


9. MOTCCR: tris(4-Morpholinedithiocarbamato)-chromium(III) dichloromethane solvate

R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans*., 1975, pp. 2517-2522; doi: 10.1039/dt9750002517

d = 3.25 Å, C–H···Cg(chelate ring) = 153° and θ = 11°

{A dithiocarbamate ligand accepts a methylene-C–H···Cg(chelate ring) interaction from the DCM molecule to a two-molecule aggregate; isostructural with manganese(III) (MOTCMN) and iron(III) analogues (MRDTFE02) analogues}

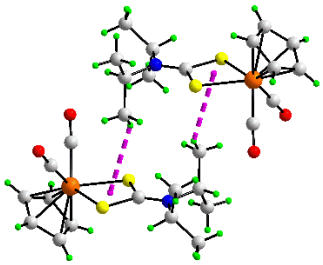


10. XUJGUE: (η^5-Cyclopentadienyl)-dicarbonyl-(dimethyldithiocarbamato)chromium(II)

L. Y. Goh, Z. Weng, W. K. Leong and P. H. Leung, *Organometallics*, 2002, **21**, 4398-4407; doi: 10.1021/om0202930

d = 2.99 Å, C–H···Cg(chelate ring) = 145° and θ = 10°

{Centrosymmetrically related molecules associate into a dimeric aggregate *via* a pair of N-methyl-C–H···Cg(chelate ring) interactions}

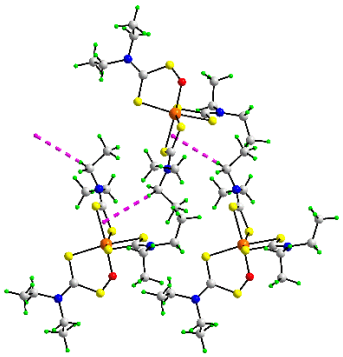


11. XUJHEP: (η^5-Cyclopentadienyl)-dicarbonyl-(diisopropyldithiocarbamato)chromium(II)

L. Y. Goh, Z. Weng, W. K. Leong and P. H. Leung, *Organometallics*, 2002, **21**, 4398-4407; doi: 10.1021/om0202930

d = 3.05 Å, C–H···Cg(chelate ring) = 130° and θ = 17°

{Centrosymmetrically related molecules associate into a dimeric aggregate *via* a pair of methyl-C–H···Cg(chelate ring) interactions}

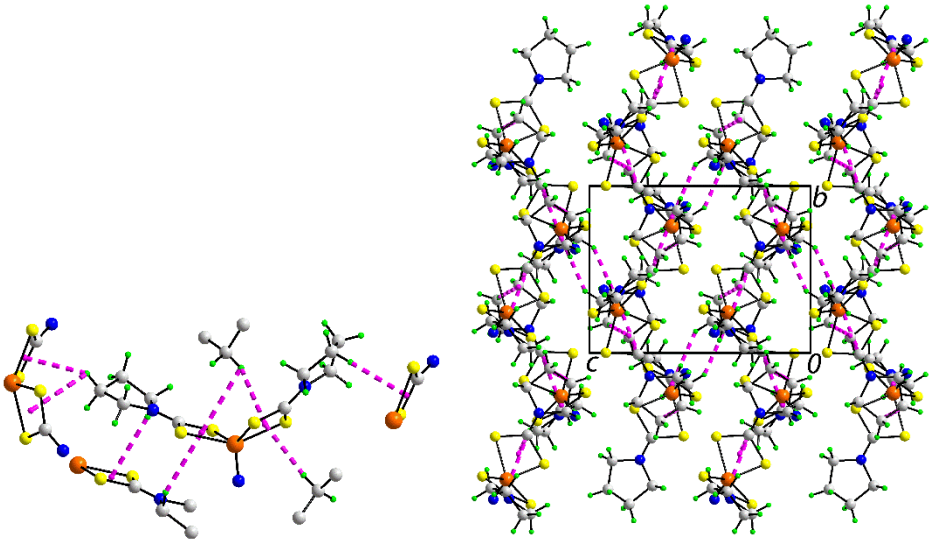


12. EDTCOR: bis(Diethyldithiocarbamato)(diethyldithioperoxycarbamato)chromium(III)

J. M. Hope, R. L. Martin, D. Taylor and A. H. White, *Chem. Commun*. 1977, pp. 99-100; doi: 10.1039/C39770000099

d = 3.17 Å, C–H···Cg(chelate ring) = 131° and θ = 18°

{A dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a helical (2_1) supramolecular chain. Hydrogen atom positions were generated in *Mercury*}



13. OMAKIW: bis(Pyrrolidinedithiocarbamato)-nitrido-chromium(V)

T. Birk and J. Bendix, *Inorg. Chem.*, 2003, **42**, 7608-7615; doi: 10.1021/ic034777f

d = 2.74 Å, C–H···Cg(chelate ring) = 131° and θ = 10°

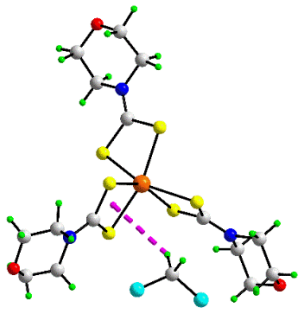
d = 3.17 Å, C–H···Cg(chelate ring) = 106° and θ = 16°

d = 2.74 Å, C–H···Cg(chelate ring) = 163° and θ = 8°

d = 2.97 Å, C–H···Cg(chelate ring) = 146° and θ = 16°

{Each dithiocarbamate ligand participates in two methylene-C–H···Cg(chelate ring) interactions within a three-dimensional architecture. A methylene-H spans two rings, first and second entries. The ring that accepts the shorter contact also accepts a contact of similar separation from another methylene-H;, third entry. The second dithiocarbamate ring accepts the fourth contact from a third methylene-H atom. Globally, the first three listed contacts assemble molecules into a supramolecular layer in the ab-plane and the last listed contact connects these into a 3-D array}

MANGANESE

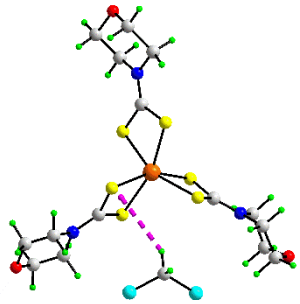


14. MOTCMN: tris(4-Morpholinedithiocarbamato)manganese(III) dichloromethane solvate

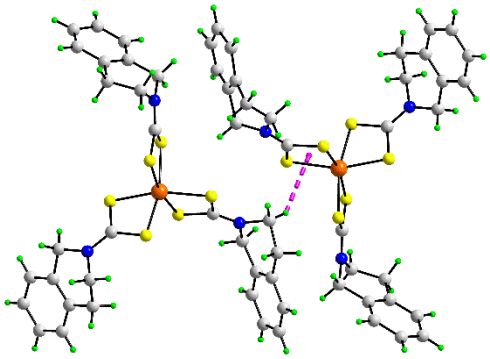
R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1975, pp. 2517-2522; doi: 10.1039/dt9750002517

d = 3.16 Å, C–H···Cg(chelate ring) = 145° and θ = 10°

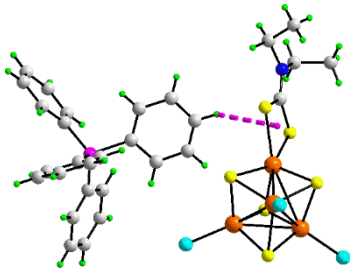
{A dithiocarbamate ligand accepts a C–H···Cg(chelate ring) from the solvent molecule. The crystal is isostructural with chromium(III) (MOTCCR) and iron(III) (MRDTFE02) analogues}



15. MRDTFE02: tris(4-Morpholinecarbodithioato)iron(III) dichloromethane solvate
K. Ståhl, *Acta Crystallogr., Sect. B: Struct .Sci.*, 1983, **39**, 612-620; doi: 10.1107/S0108768183003067
d = 2.92 Å, C–H···Cg(chelate ring) = 150° and θ = 10°
{A dithiocarbamate ligand accepts a methylene-C–H···Cg(chelate ring) interaction from the solvent molecule. The crystal is isostructural with the manganese(III) (MOTCCR) and chromium(III) (MOTCMN) analogues}

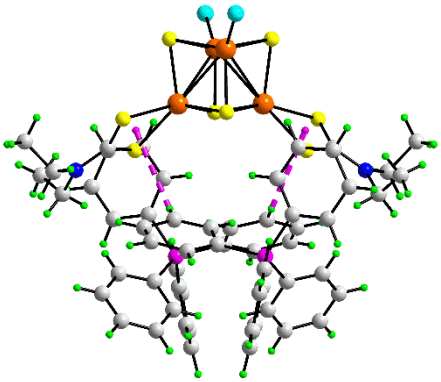


16. ZAGZIT: tris(3,4-Dihydroisoquinoline-2(1H)-carbodithioato)iron(III)
S. Mlowe, D. J. Lewis, M. A. Malik, J. Raftery, E. B. Mubofu, P. O'Brien and N. Revaprasadu, *Dalton Trans.*, 2016, **45**, 2647-2655; doi: 10.1039/C5DT03881B
d = 3.03 Å, C–H···Cg(chelate ring) = 142° and θ = 11°
{Two independent molecules in the asymmetric unit. These are connected into a two-molecule aggregate by a single N-methylene-C–H···Cg(chelate ring) interaction}

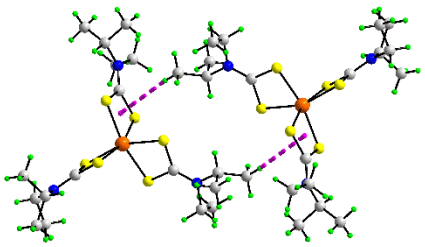


17. DAMPAI: bis(Tetraphenylphosphonium) trichloro-diethyldithiocarbamato-tetrakis(μ$_3$-sulfido)-tetra-iron(II,III) dimethylformamide solvate
M. G. Kanatzidis, D. Coucouvanis, A. Simopoulos, A. Kostikas and V. Papaefthymiou, *J. Am. Chem. Soc.*, 1985, **107**, 4925-4935; doi: 10.1021/ja00303a018
d = 3.08 Å, C–H···Cg(chelate ring) = 137° and θ = 18°

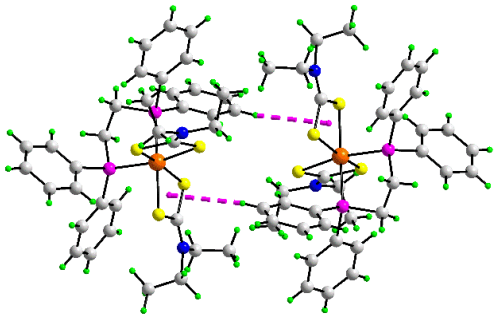
{The dithiocarbamate ligand in the tetra-iron cluster, lacking symmetry, accepts a phenyl-C–H···Cg(chelate ring) interaction provided by one of the tetraphenylphosphonium counter-ions to form a two-ion aggregate}



18. DAMNUA: bis(Tetraphenylphosphonium) dichloro-bis(diethyldithiocarbamato)-tetrakis(μ_3-sulfido)-tetra-iron(II,III)
M. G. Kanatzidis, D. Coucouvanis, A. Simopoulos, A. Kostikas and V. Papaefthymiou, *J. Am. Chem. Soc*., 1985, **107**, 4925-4935; doi: 10.1021/ja00303a018
d = 3.04 Å, C–H···Cg(chelate ring) = 126° and θ = 17°
{The tetra-iron cluster has two-fold symmetry. Each chelate ring accepts a phenyl-C–H···Cg(chelate ring) interaction provided by a tetraphenylphosphonium counter-ion to form a three-ion aggregate}



19. UTIDOR: tris[Ethyl(isopropyl)carbamodithioato]iron(III)
M. Akhtar, J. Akhter, M. A. Malik, P. O'Brien, F. Tuna, J. Raftery and M. Helliwell, *J. Mater. Chem*., 2011, **21**, 9737-9745; doi: 10.1039/c1jm10703h
d = 3.14 Å, C–H···Cg(chelate ring) = 170° and θ = 19°
{Two molecules self-associate about a centre of inversion to form a dimeric aggregate *via* a pair of methyl-C–H···Cg(chelate ring) interactions}

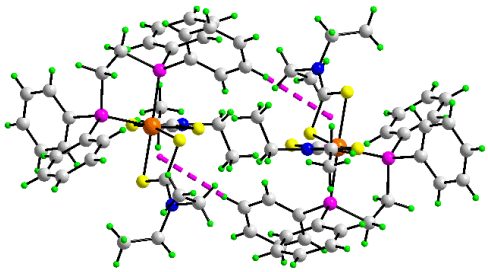


20. KUBPED: bis(Diethyldithiocarbamato)-(1,2-bis(diphenylphosphino)ethane)-iron(III) tetrachlorido-iron(III)

T. K. Jana, D. P. Kumar, R. Pradhan, S. Dinda, P. N. Ghosh, C. Simonnet, J. Marrot, I. Imaz, A. Wattiaux, L. Fournes, J.-P. Sutter, F. Secheresse and R. Bhattacharyya, *Inorg. Chim. Acta*, 2009, **362**, 3583-3594; doi: 10.1016/j.ica.2009.04.007

d = 3.28 Å, C–H···Cg(chelate ring) = 169° and θ = 17°

{Two molecules self-associate about a centre of inversion to form a dimeric aggregate *via* a pair of phenyl-C–H···Cg(chelate ring) interactions}

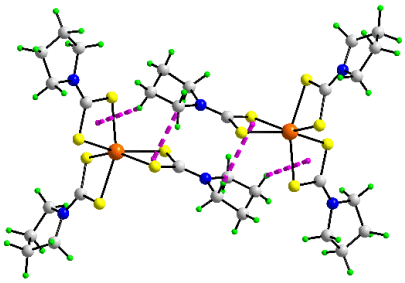


21. KUBPIH: bis(Diethyldithiocarbamato)-(1,2-bis(diphenylphosphino)ethane)-iron(III) tetraphenylborate

T. K. Jana, D. P. Kumar, R. Pradhan, S. Dinda, P. N. Ghosh, C. Simonnet, J. Marrot, I. Imaz, A. Wattiaux, L. Fournes, J.-P. Sutter, F. Secheresse and R. Bhattacharyya, *Inorg. Chim. Acta*, 2009, **362**, 3583-3594; doi: 10.1016/j.ica.2009.04.007

d = 3.29 Å, C–H···Cg(chelate ring) = 160° and θ = 19°

{There are two independent molecules. One of the molecules self-associates about a centre of inversion to form a dimeric aggregate *via* a pair of phenyl-C–H···Cg(chelate ring) interactions }



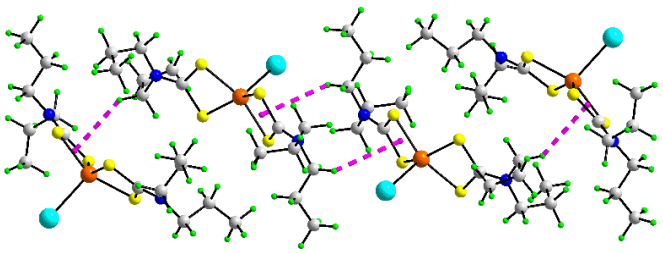
22. PYCDFE10: tris(Pyrrolidine-1-carbodithioato)iron(III)

S. Mitra, C. L. Raston and A. H. White, *Aust. J. Chem*., 1978, **31**, 547-553; doi: 10.1071/CH9780547

d = 3.11 Å, C–H···Cg(chelate ring) = 152° and θ = 16°

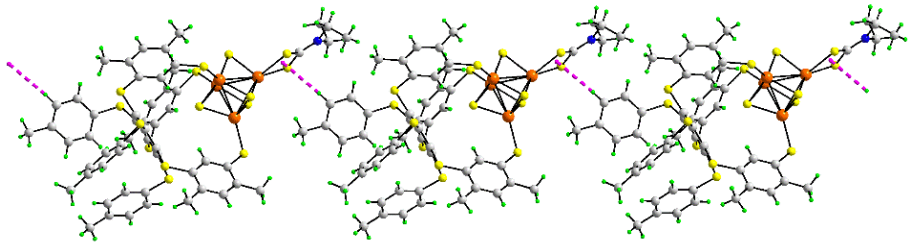
d = 3.14 Å, C–H···Cg(chelate ring) = 142° and θ = 14°

{Two molecules self-associate about a centre of inversion to form a dimeric aggregate *via* a pair of N-methylene-C–H···Cg(chelate ring), first entry, and a pair of methylene-C–H···Cg(chelate ring) interactions}

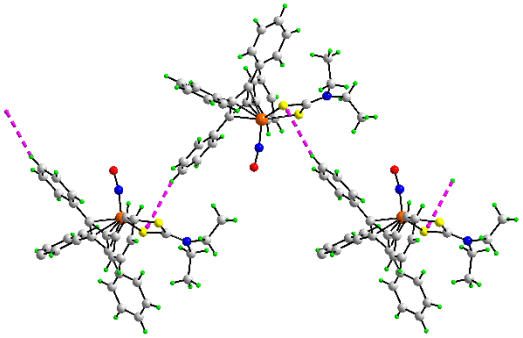


23. GEDTUE: Iodo-bis(di-*n*-propyldithiocarbamato)iron(III)

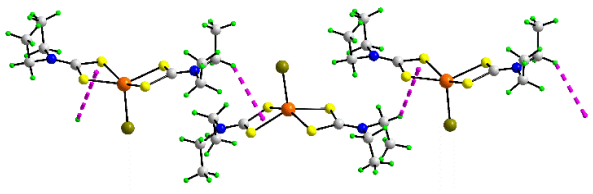
B. E. A. Abadi, R. A. Palmer and B. W. Fitzsimmons, *J. Crystallogr. Spectrosc. Res*., 1988, **18**, 35-53; doi: 10.1007/BF01171023
d = 2.99 Å, C–H···Cg(chelate ring) = 127° and θ = 11°
d = 3.25 Å, C–H···Cg(chelate ring) = 138° and θ = 10°
{There are two independent molecules. One of these self-associates about a centre of inversion to form a dimeric aggregate *via* a pair of N-methylene-C–H···Cg(chelate ring) interactions. Attached to this *via* two terminal N-methylene-C–H···Cg(chelate ring) interactions are two of the second independent molecules so that a four-molecule aggregate is formed}



24. POBNUR: bis(Tetraphenylphosphonium) tetrakis(μ$_3$-sulfido)-(μ$_3$-3,3'-((5-((2,4-dimethyl-5-sulfanylphenyl)sulfanyl)-2,4,6-tris((4-methylphenyl)sulfanyl)-1,3-phenylene)disulfanediyl)bis(4,6-dimethylbenzenethiolate))-(diethylcarbamodithioato)-tetra-iron diethyl ether solvate
E. Victor and S. J. Lippard, *Inorg. Chem*., 2014, **53**, 5311-5320; doi: 10.1021/ic500586g
d = 2.94 Å, C–H···Cg(chelate ring) = 167° and θ = 19°
{Each molecule accepts and donates a phenyl-C–H···Cg(chelate ring) interaction to form a linear supramolecular chain}

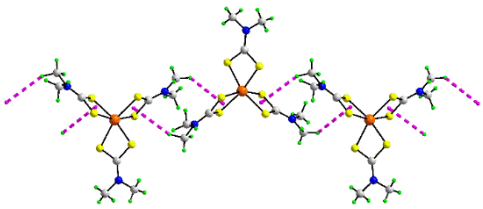


25. CEHFOK: (Diethyldithiocarbamato)-nitrosyl-(η^4-tetraphenylcyclobutadiene)-iron(0)
L. F. J. Lalor, L. H. Brookes, G. Ferguson and M. Parvez, *J. Chem. Soc., Dalton Trans*., 1984, pp. 245-248; doi: 10.1039/dt9840000245
d = 3.09 Å, C–H···Cg(chelate ring) = 145° and θ = 14°
{Each molecule donates and accepts a phenyl-C–H···Cg(chelate ring) interaction to generate a supramolecular chain with helical topology, being propagated by screw (2$_1$) symmetry}

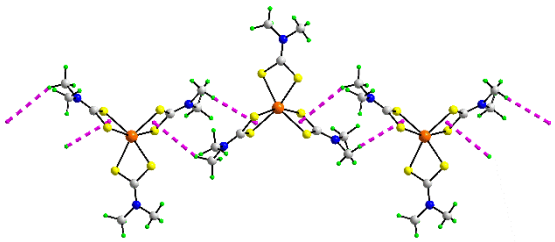


26. DTCFEB01: Bromido-bis(diethyldithiocarbamato)-iron(III)
S. Decurtins, C. B. Shoemaker and H. H. Wickman, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., 1983, **39**, 1218-1221; doi: 10.1107/S0108270183007994

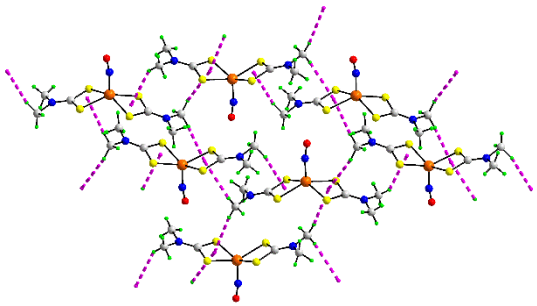
d = 3.12 Å, C–H···Cg(chelate ring) = 138° and θ = 11°
{Each molecule accepts and donates a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a zig-zag topology (glide symmetry)}



27. DMTCFE02: tris(Dimethyldithiocarbamato)iron(III) - low-spin form
J. Albertsson, Å. Oskarsson, K. Ståhl, C. Svensson and I.Ymén, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1981, **37**, 50-56; doi: 10.1107/S0567740881002173
d = 3.00 Å, C–H···Cg(chelate ring) = 131° and θ = 14°
d = 3.04 Å, C–H···Cg(chelate ring) = 157° and θ = 18°
{Each molecule accepts and donates two N-methyl-C–H···Cg(chelate ring) interactions to form a supramolecular chain with a zig-zag topology (glide symmetry)}

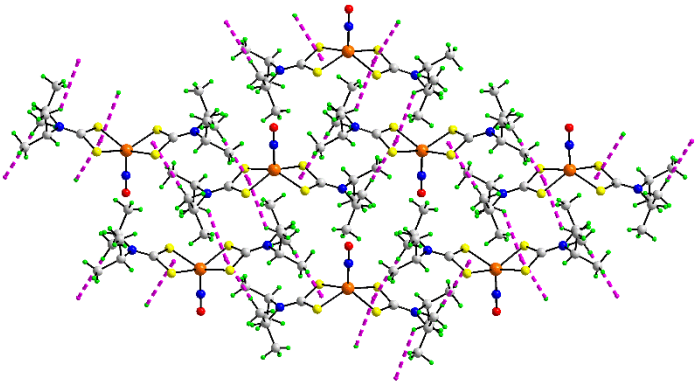


28. DMTCFE03: tris(Dimethyldithiocarbamato)iron(III) - high-spin form
J. Albertsson, Å. Oskarsson, K. Ståhl, C. Svensson and I.Ymén, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1981, **37**, 50-56; doi: 10.1107/S0567740881002173
d = 3.19 Å, C–H···Cg(chelate ring) = 134° and θ = 15°
d = 3.30 Å, C–H···Cg(chelate ring) = 155° and θ = 18°
{Each molecule accepts and donates two N-methyl-C–H···Cg(chelate ring) interactions to form a supramolecular chain with a zig-zag topology (glide symmetry)}

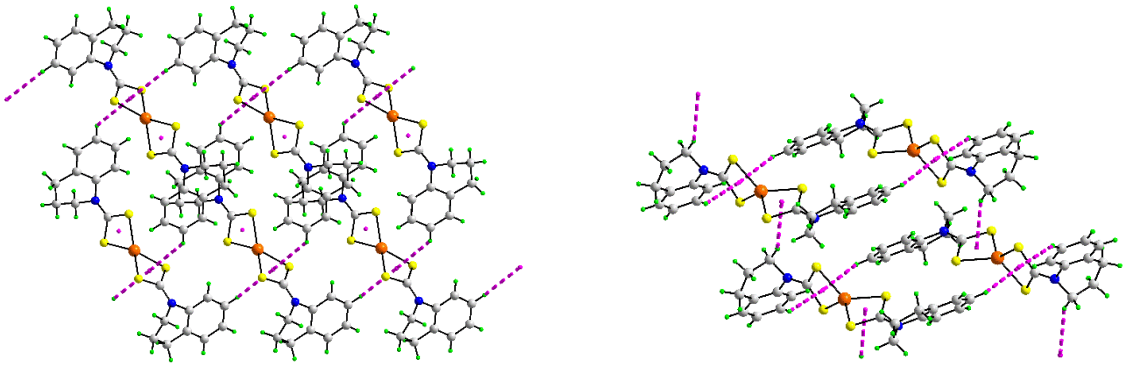


29. FEDMDT01: bis(Dimethyldithiocarbamato)-nitrosyl-iron(III)
G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais and P. G. Owston, *J. Chem. Soc. A*, 1970, pp. 1275-1283; doi: 10.1039/j19700001275
d = 2.85 Å, C–H···Cg(chelate ring) = 170° and θ = 7°
d = 3.03 Å, C–H···Cg(chelate ring) = 149° and θ = 19°
d = 2.78 Å, C–H···Cg(chelate ring) = 145° and θ = 10°
{One dithiocarbamate ligands forms two N-methyl-C–H···Cg(chelate ring) interactions, entries one and two, with symmetry related rings being effectively bridged by methyl groups employing two methyl-

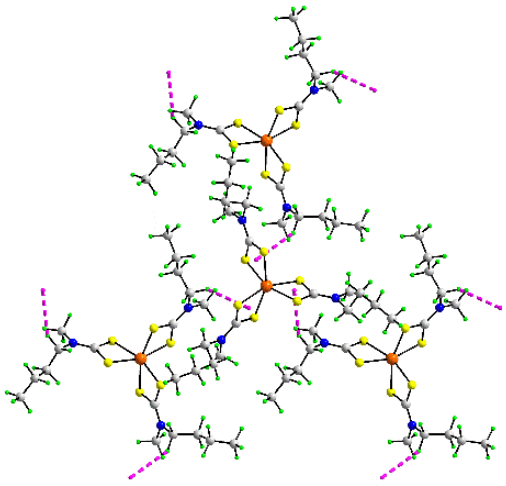
H atoms. One methyl group of this ring connects to the other dithiocarbamate ligand *via* a N-methyl-C–H···Cg(chelate ring) interaction, entry three, so that a 2-D grid results}



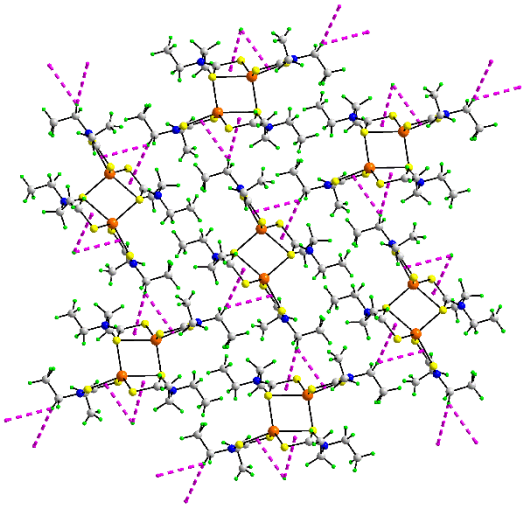
30. PRCBFE: Nitrosyl-bis(diisopropyl-dithiocarbamato)iron(III)
R. J. Butcher and E. Sinn, *Inorg. Chem*., 1980, **19**, 3622-3626; doi: 10.1021/ic50214a012
d = 2.85 Å, C–H···Cg(chelate ring) = 156° and θ = 8°
d = 3.15 Å, C–H···Cg(chelate ring) = 133° and θ = 9°
d = 3.13 Å, C–H···Cg(chelate ring) = 148° and θ = 11°
{One dithiocarbamate ligand forms two methyl-C–H···Cg(chelate ring) interactions donated from two symmetry related molecules; entries one and two. One methyl group of this ring connects to the other dithiocarbamate ligand *via* a methyl-C–H···Cg(chelate ring) interaction so that a 2-D grid results}



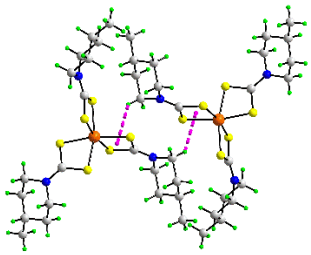
31. WEBZAH: bis(3,4-Dihydroquinoline-1(2H)-carbodithioato)iron(II)
S. Saeed, R. Hussain and R. J. Butcher, *J. Coord. Chem*., 2014, **67**, 1693-1701; doi: 10.1080/00958972.2014.918265
d = 3.08 Å, C–H···Cg(chelate ring) = 147° and θ = 12°
d = 3.08 Å, C–H···Cg(chelate ring) = 137° and θ = 7°
d = 3.09 Å, C–H···Cg(chelate ring) = 155° and θ = 14°
{Both dithiocarbamate ligands engage in C–H···Cg(chelate ring) interactions. One ring accepts two phenyl-C–H···Cg(chelate ring) interaction and donates phenyl-H atoms from both ligands to generate a supramolecular tube. Tubes are assembled into a layer by forming N-methylene-C–H···Cg(chelate ring) interactions on either side to form a supramolecular double-layer}



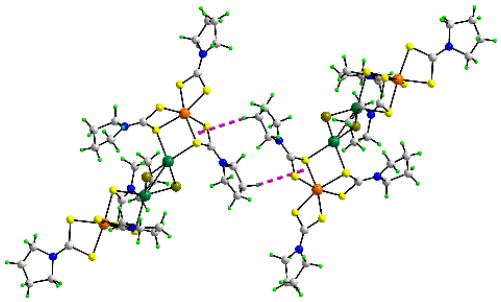
32. CEXXIM: tris(N-Methyl-N-n-butyldithiocarbamato)iron(III)
A. Terzis, S. Filippakis, D. Mentzafos, V. Petrouleas and A. Malliaris, *Inorg. Chem*. 1984, **23**, 334-337; doi: 10.1021/ic00171a013
d = 3.00 Å, C–H···Cg(chelate ring) = 142° and θ = 14°
{There are two crystallographically independent molecules, each with 3-fold symmetry. In one of the independent molecule, each dithiocarbamate chelate ring functions as an acceptor of a N-methylene-C–H···Cg(chelate ring) interaction whereas the other is a provider of three such contacts. The interactions occur laterally to form a supramolecular layer with a flat topology}



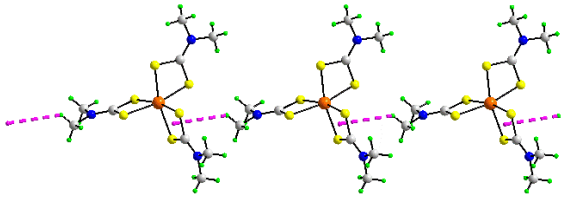
33. EDTCFD: bis[(μ$_2$-Diethyldithiocarbamato)-bis(diethyldithiocarbamato)-iron(II)]
O. A. Ileperuma and R. D. Feltham, *Inorg. Chem*., 1975, **14**, 3042-3045; doi: 10.1021/ic50154a037
d = 3.14 Å, C–H···Cg(chelate ring) = 162° and θ = 16°
d = 3.21 Å, C–H···Cg(chelate ring) = 113° and θ = 17°
{Each centrosymmetric binuclear molecule accepts and donates two N-methylene-C–H···Cg(chelate ring) interactions from a single methylene-H donor to form a supramolecular 2-D array}



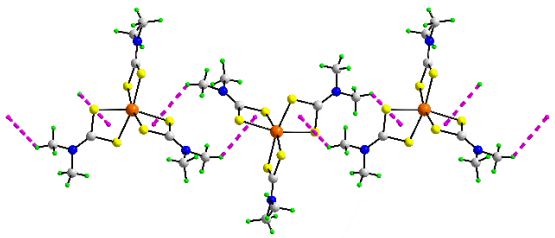
34. EWESOQ: tris(4-Methylpiperidine-1-carbodithioato)cobalt(III) chloroform solvate
P. Nath, M. K. Bharty, B. Maiti, A. Bharti, R. J. Butcher, J. L. Wikaira and N. K. Singh, *RSC Advances*, 2016, **6**, 93867-93880; doi: 10.1039/C6RA15186H
d = 3.16 Å, C–H···Cg(chelate ring) = 140° and θ = 17°
{Centrosymmetrically related molecules are connected into a dimeric aggregate *via* a pair methylene-C–H···π(chelate ring) interactions}



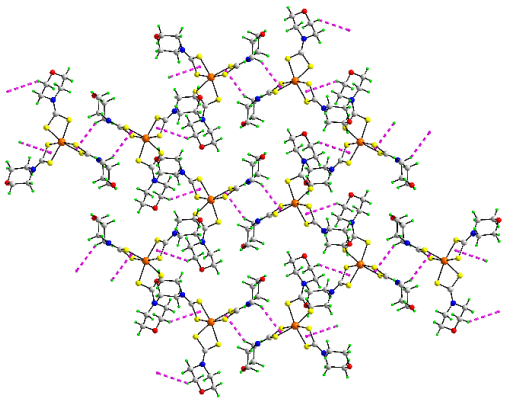
35. CUVCEB: bis[(μ$_2$-Bromo)-tris(pyrrolidinecarbodithioato)-cobalt(III)]-di-copper(I)
L. M. Engelhardt, P. C. Healy, R. I. Papasergio and A. H. White, *Inorg. Chem*., 1985, **24**, 382-385; doi: 10.1021/ic00197a027
d = 3.28 Å, C–H···Cg(chelate ring) = 153° and θ = 16°
Centrosymmetrically related molecules are connected into a dimeric aggregate *via* a pair methylene-C–H···π(chelate ring) interactions}



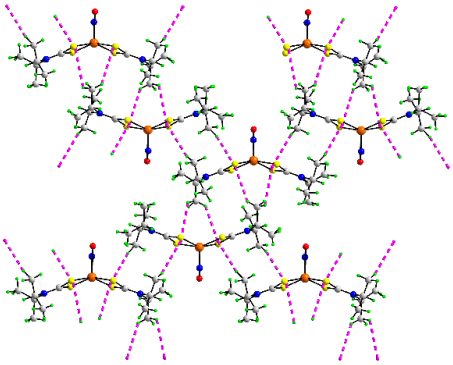
36. VIQFEH: tris(Dimethyldithiocarbamato)cobalt(III) iodine hemi-solvate
N. V. Khitrich, I. I. Seifullina, S. E. Nefedov and A. V. Mazepa, *Russ. J. Inorg. Chem*., 2006, **51**, 1000-1008.
d = 3.24 Å, C–H···Cg(chelate ring) = 133° and θ = 17°
{Each dithiocarbamate ligand accepts N-methyl-C–H···π(chelate ring) interaction to form a linear supramolecular chain}



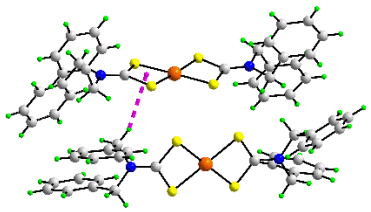
37. MUJBIC: tris(Dimethyldithiocarbamato)cobalt(III) bis(di-iodine)
N. V. Khitrich, I. I. Seifullina and Z. A. Starikova, *Russ. J. Inorg. Chem*., 2002, **47**, 80-86.
d = 3.07 Å, C–H···Cg(chelate ring) = 132° and θ = 18°
{The $Co(dtc)_3$ molecule has 2-fold symmetry. Each of the symmetry related dithiocarbamate ligands accepts a methyl-C–H···π(chelate ring) interaction to form a zig-zag supramolecular chain (glide symmetry}



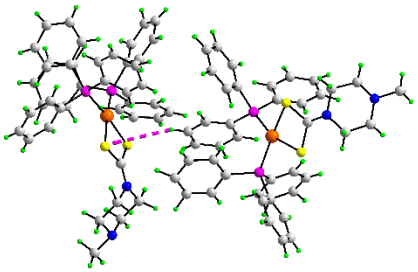
38. UDUWAS: tris(4-Morpholinecarbodithioato)cobalt(III)
A. Kropidlowska, J. Chojnacki, J. Golaszewska, D. Paliwoda and B. Becker, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m2117; doi: 10.1107/S160053680703276X
d = 2.99 Å, C–H···Cg(chelate ring) = 152° and θ = 17°
d = 3.22 Å, C–H···Cg(chelate ring) = 131° and θ = 15°
{Two distinct methylene-C–H···π(chelate ring) interactions, involving two different dithiocarbamate ligands, occur in the molecular packing. The shorter of these connect centrosymmetrically related molecules into a dimeric aggregate, *i.e. via* N-methylene-C–H···π(chelate ring) interactions. The dimers are connected into a two-dimensional array by the longer O-methylene-C–H···π(chelate ring) interactions}



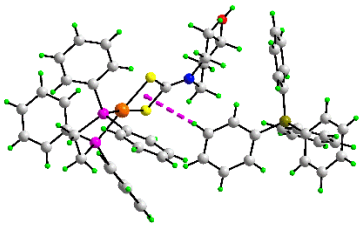
39. BUBBAB: bis(Diisopropyldithiocarbamato)-nitrosyl-cobalt(III)
G. A. Brewer, R. J. Butcher, B. Letafat and E. Sinn, *Inorg. Chem*., 1983, **22**, 371-375; doi: 10.1021/ic00145a001
d = 3.12 Å, C–H···Cg(chelate ring) = 136° and θ = 8°
{Centrosymmetrically related molecules are connected into a dimeric aggregate *via* four methyl-C–H···π(chelate ring) interactions whereby a methyl group of one molecule connects to two dithiocarbamate ligands of the other molecule employing two hydrogen atoms. The dimeric aggregates are connected into a two-dimensional array *via* two additional methyl-C–H···π(chelate ring) interactions per molecule, derived from two different methyl substituents so that each dithiocarbamate ligand forms two methyl-C–H···π(chelate ring) interactions}



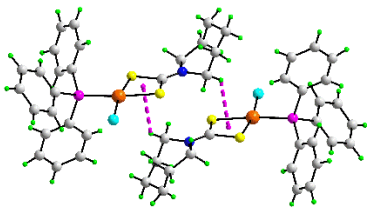
40. PADKIQ: bis(Dibenzylcarbamodithioato)nickel(II)
B. Cvek, V. Milacic, J. Taraba and Q. P. Dou, *J. Med. Chem.*, 2008, **51**, 6256-6258; doi: 10.1021/jm8007807
d = 2.97 Å, C–H···Cg(chelate ring) = 159° and θ = 18°
{A single N-methylene-C–H···Cg(chelate ring) interaction connects the two independent molecules comprising the asymmetric unit}



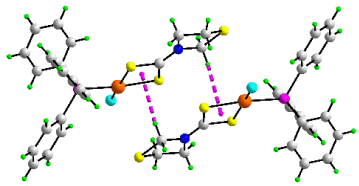
41. CIBDEX: (4-Methylpiperazinecarbodithioato)-bis(triphenylphosphine)-nickel(II) perchlorate monohydrate
B. A. Prakasam, K. Ramalingam, R. Baskaran, G. Bocelli and A. Cantoni, *Polyhedron*, 2007, **26**, 1133-1138; doi: 10.1016/j.poly.2006.10.006
d = 3.15 Å, C–H···Cg(chelate ring) = 153° and θ = 19°
{A single phosphino-bound phenyl-C–H···Cg(chelate ring) interaction connects the two independent cations comprising the asymmetric unit into a two-molecule aggregate}



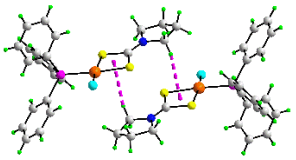
42. BOGBIK: (Ethane-1,2-diylbis(diphenylphosphino))-(4-hydroxypiperidine-1-carbodithioato)-nickel(II) tetraphenylborate dichloromethane solvate
R. Chauhan, M. Trivedi, J. Singh, K. Molloy, G. Kociok-Köhn, U. Mulik, D. Amalnerkar and A. Kumar, *Inorg. Chim. Acta*, 2014, **415**, 69-74; doi: 10.1016/j.ica.2014.02.038
d = 3.13 Å, C–H···Cg(chelate ring) = 124° and θ = 18°
{A single tetraphenylborate-bound phenyl-C–H···Cg(chelate ring) interaction connects the cation to the anion to form a two-molecule aggregate}



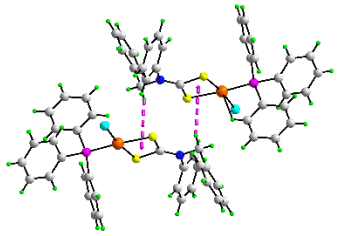
43. TACBUV: Chlorido-triphenylphosphino-(hexamethylenedithiocarbamato)-nickel(II) chloroform solvate
M. Pavlíček, Z. Trávníček, R. Pastorek and J. Marek, *Transition Met. Chem.*, 2003, **28**, 260-264; doi: 10.1023/A:1022932706275
d = 2.87 Å, C–H···Cg(chelate ring) = 129° and θ = 2°
{About a centre of inversion, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



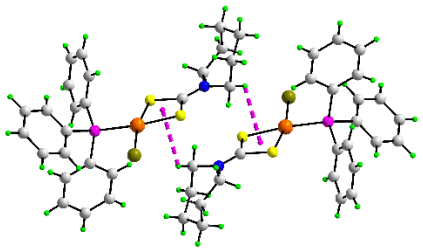
44. GOZBUS: Chlorido-(thiazolidinedithiocarbamato)-(triphenylphosphino)-nickel(II) chloroform solvate
R. Pastorek, Z. Trávníček, E. Kvapilova, Z. Šindelar, F. Březina and J. Marek, *Polyhedron*, 1999, **18**, 151-157; doi: 10.1016/S0277-5387(98)00279-4
d = 2.98 Å, C–H···Cg(chelate ring) = 141° and θ = 2°
{About a centre of inversion, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



45. WIHCOG: Chlorido-(1-pyrrolidinecarbodithioato)-(triphenylphosphine)-nickel(II) chloroform solvate
A. Kropidłowska, J. Janczak, J. Gołaszewska and B. Becker, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1947; doi: 10.1107/S1600536807027791
d = 3.00 Å, C–H···Cg(chelate ring) = 152° and θ = 9°
{About a centre of inversion, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



46. TADKOB: [Benzyl(phenyl)carbamodithioato]-chlorido-(triphenylphosphino)-nickel(II)
J. Masnovi, N. V. Duffy, P. E. Fanwick and A. F. Hepp, *J. Coord. Chem.*, 2016, **69**, 90-102; doi: 10.1080/00958972.2015.1107904
d = 3.17 Å, C–H···Cg(chelate ring) = 124° and θ = 9°
{About a centre of inversion, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

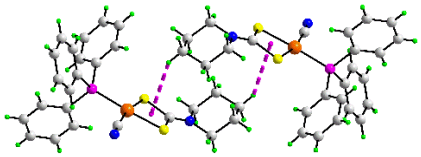


47. TACCAC: Bromido-triphenylphosphino-(hexamethylenedithiocarbamato)-nickel(II) chloroform solvate

M. Pavlíček, Z. Trávníček, R. Pastorek and J. Marek, *Transition Met. Chem.*, 2003, **28**, 260-264; doi: 10.1023/A:1022932706275

d = 2.97 Å, C–H···Cg(chelate ring) = 113° and θ = 11°

{About a centre of inversion, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

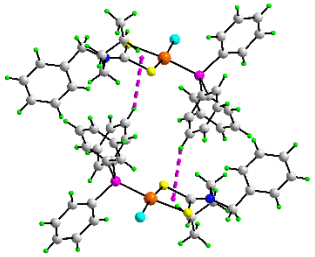


48. WAYJOX: Cyano-(triphenylphosphino)-(piperidine-1-carbodithioato)-nickel(II) acetonitrile solvate

K. Ramalingam, R. Thiruneelakandan, G. Bocelli and L. Righi, *Central Eur. J. Chem.*, 2012, **10**, 1199-1207; doi: 10.2478/s11532-012-0041-2

d = 3.30 Å, C–H···Cg(chelate ring) = 141° and θ = 8°

{About a centre of inversion, each dithiocarbamate ligand accepts a methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

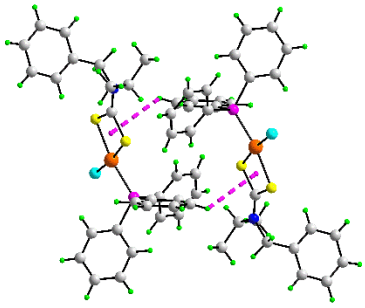


49. KICDUW: (N-Benzyl-N-(n-butyl)dithiocarbamato)-chlorido-(triphenylphosphino)-nickel(II)

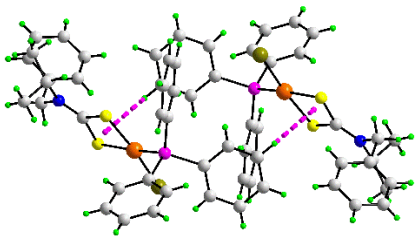
R. Pastorek, J. Kameníček, J. Husárek, V. Slovak and M. Pavlíček, *J. Coord. Chem.*, 2007, **60**, 485-494; doi: 10.1080/00958970600794966

d = 3.13 Å, C–H···Cg(chelate ring) = 148° and θ = 11°

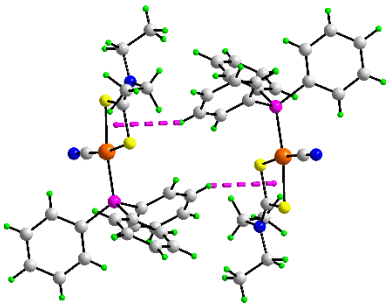
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



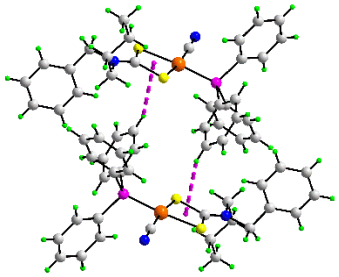
50. HOTXAP: Chlorido-(triphenylphosphino)-(benzylisopropyldithiocarbamato)-nickel(II) chloroform solvate
R. Pastorek, J. Kameníček, Z. Trávníček, J. Husárek and N. Duffy, *Polyhedron*, 1999, **18**, 2879-2883; doi: 10.1016/S0277-5387(99)00188-6
d = 3.29 Å, C–H···Cg(chelate ring) = 119° and θ = 18°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



51. HOTXET: Bromido-(triphenylphosphino)-(benzylisopropyldithiocarbamato)-nickel(II)
R. Pastorek, J. Kameníček, Z. Trávníček, J. Husárek and N. Duffy, *Polyhedron*, 1999, **18**, 2879-2883; doi: 10.1016/S0277-5387(99)00188-6
d = 2.93 Å, C–H···Cg(chelate ring) = 131° and θ = 17°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

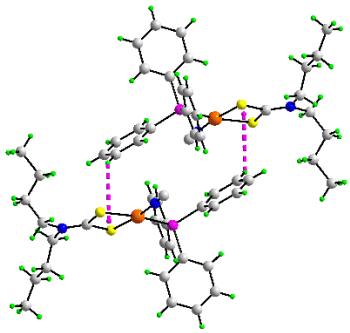


52. FAVZUY: Cyano-(diethyldithiocarbamato)-(triphenylphosphino)-nickel(II)
R. Thiruneelakandan, K. Ramalingam, G. Bocelli and L. Righi, *Z. Anorg. Allg. Chem.*, 2005, **631**, 187-193; doi: 10.1002/zaac.200400245
d = 3.12 Å, C–H···Cg(chelate ring) = 140° and θ = 2°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

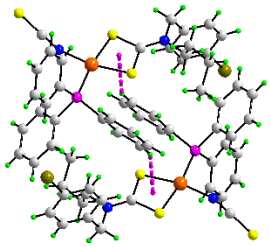


53. YOMBOT: [Benzyl(butyl)carbamodithioato]-(cyano)-(triphenylphosphino)-nickel(II)
B. A. Prakasam, M. Lahtinen, A. Peuronen, M. Muruganandham, E. Kolehmainen, E. Haapaniemi, and M. Sillanpää, *Polyhedron*, 2014, **81**, 588-596; doi: 10.1016/j.poly.2014.06.059
d = 3.13 Å, C–H···Cg(chelate ring) = 146° and θ = 10°

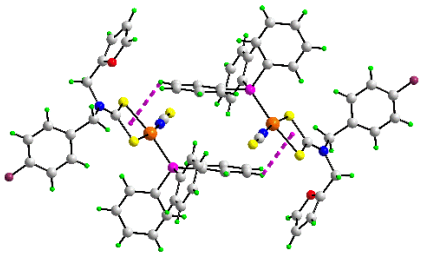
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



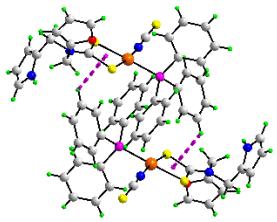
54. IFEZID: (Di-n-butyldithiocarbamato)-isocyanido-(triphenylphosphino)-nickel(II)
R. Bhaskaran, K. Ramalingam, G. Bocelli, A. Cantoni and C. Rizzoli, *J. Coord. Chem.*, 2008, **61**, 1710-1719; doi: 10.1080/00958970701761898
d = 3.03 Å, C–H···Cg(chelate ring) = 124° and θ = 15°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



55. HAMLUF: [(4-Bromobenzyl)butylcarbamodithioato]-isothiocyanato-triphenylphosphino-nickel(II)
B. A. Prakasam, A. Peuronen, M. Lahtinen, M. Muruganandham, E. Kolehmainen, E. Haapaniemi and M. Sillanpää, *Polyhedron*, 2017, **123**, 453-461; doi: 10.1016/j.poly.2016.11.027
d = 2.78 Å, C–H···Cg(chelate ring) = 148° and θ = 6°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



56. USAROX: [(4-Fluorobenzyl)(2-furylmethyl)carbamodithioato]-(isothiocyanato)-(triphenylphosphino)-nickel(II)
E. Sathiyaraj, S. Thirumaran and S. Ciattini, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 2016, **191**, 1042-1050; doi: 10.1080/10426507.2015.1135150
d = 2.96 Å, C–H···Cg(chelate ring) = 123° and θ = 14°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

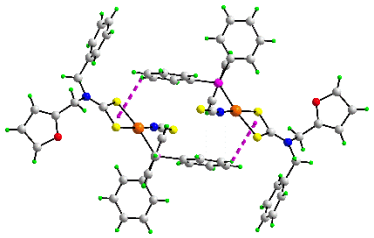


57. TUJYEE: [(2-Furylmethyl)(1H-pyrrol-2-ylmethyl)carbamodithioato]-(isothiocyanato)-(triphenylphosphino)-nickel(II)

E. Sathiyaraj, G. Gurumoorthy and S. Thirumaran, *New J. Chem.*, 2015, **39**, 5336-5349; doi: 10.1039/C4NJ02250E

d = 2.97 Å, C–H···Cg(chelate ring) = 124° and θ = 13°

{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

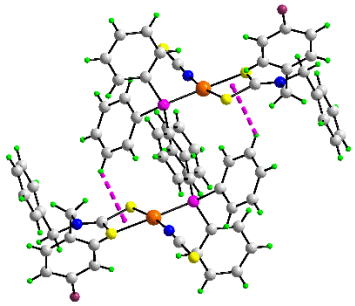


58. TOPMES: (N-Benzyl-N-furfuryldithiocarbamato)-(thiocyanato)-(triphenylphosphino)-nickel(II)

P. Valarmathi, S. Thirumaran, L. Sarmal and R. Kant, *Spectrochim. Acta, Part A*, 2014, **129**, 285-292; doi: 10.1016/j.saa.2014.03.068

d = 2.99 Å, C–H···Cg(chelate ring) = 127° and θ = 12°

{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}

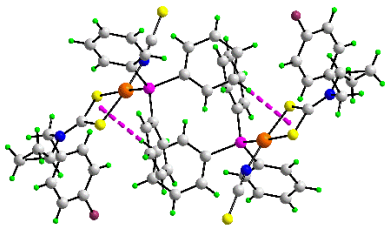


59. DEWJOH: (Butyl(4-methylbenzyl)carbamodithioato)-isothiocyanato-triphenylphosphino-nickel(II)

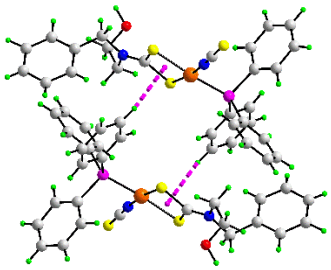
E. Sathiyaraj, S. Thirumaran, S. Selvanayagam, B. Sridhar and S. Ciattini, *J. Mol. Struct*., 2018, **1159**, 156-166; doi: 10.1016/j.molstruc.2018.01.038

d = 3.01 Å, C–H···Cg(chelate ring) = 128° and θ = 12°

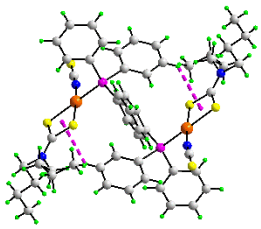
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



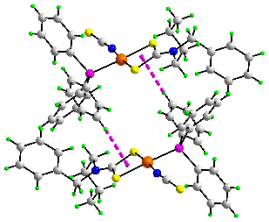
60. ZUNQIK: [N-Cyclopropyl-N-(4-fluorobenzyl)dithiocarbamate]-(isothiocyanato)-(triphenylphosphino)-nickel(II)
E. Sathiyaraj, T. Srinivasan, S. Thirumaran and D. Velmurugan, *J. Mol. Struct*., 2015, **1102**, 203-209; doi: 10.1016/j.molstruc.2015.08.053
d = 3.06 Å, C–H···Cg(chelate ring) = 130° and θ = 13°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



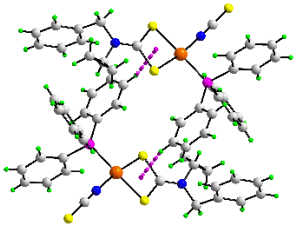
61. QOXKIY: [N-Benzyl-N-(2-hydroxyethyl)carbamodithioato]-(isothiocyanato-N)-(triphenylphosphino)-nickel(II)
R. Baskaran, K. Ramalingam, R. Thiruneelakandan, B. A. Prakasam, G. Bocelli and A. Cantoni, *J. Coord. Chem.*, 2009, **62**, 1076-1085; doi: 10.1080/00958970802483624
d = 3.08 Å, C–H···Cg(chelate ring) = 139° and θ = 13°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



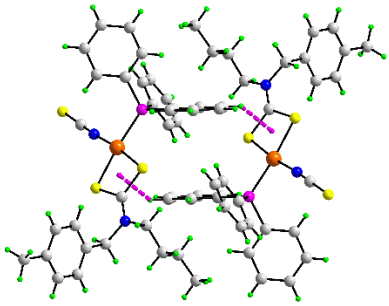
62. TOJQOY01: (Di-n-butyldithiocarbamato)-isothiocyanato-(triphenylphosphino)-nickel(II)
R. Bhaskaran, K. Ramalingam, G. Bocelli, A. Cantoni and C. Rizzoli, *J. Coord. Chem*., 2008, **61**, 1710-1719; doi: 10.1080/00958970701761898
d = 3.14 Å, C–H···Cg(chelate ring) = 126° and θ = 16°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



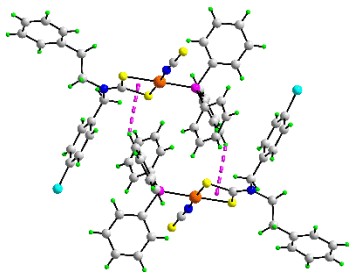
63. YOMBIN: [Benzyl(butyl)carbamodithioato]-(isothiocyanato)-(triphenylphosphino)-nickel(II)
B. A. Prakasam, M. Lahtinen, A. Peuronen, M. Muruganandham, E. Kolehmainen, E. Haapaniemi, and M. Sillanpää, *Polyhedron*, 2014, **81**, 588-596; doi: 10.1016/j.poly.2014.06.059
d = 3.15 Å, C–H···Cg(chelate ring) = 137° and θ = 8°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



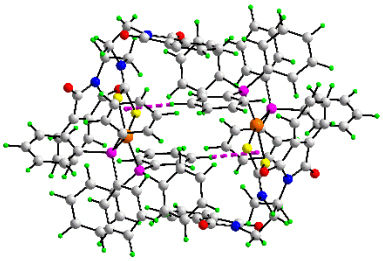
64. PUTRED: [Benzyl(cyclopropyl)carbamodithioato]-thiocyanato-triphenylphosphino-nickel(II)
E. Sathiyaraj, P. Valarmathi, S. Thirumaran, S. Ciattini, V. K. Gupta and R. Kant, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 2015, **190**, 1127-1137; doi: 10.1080/10426507.2014.976337
d = 3.17 Å, C–H···Cg(chelate ring) = 141° and θ = 5°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



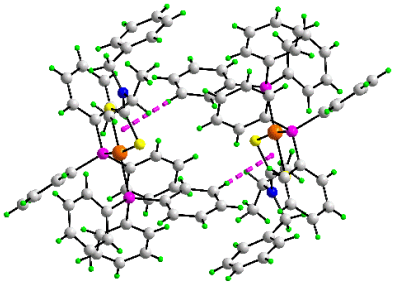
65. DACXEN: (Butyl(4-methylbenzyl)carbamodithioato)-isothiocyanato-triphenylphosphino-nickel(II)
B. A. Prakasam, A. Peuronen, M. Lahtinen, M. Muruganandham, E. Kolehmainen, E. Haapaniemi and M. Sillanpää, *Polyhedron*, 2017, **153**, 453-461; doi: 10.1016/j.poly.2016.11.027
d = 3.17 Å, C–H···Cg(chelate ring) = 136° and θ = 8°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



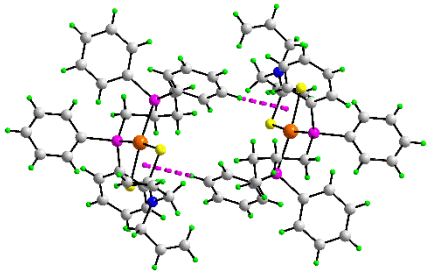
66. ULUZAE: [(4-chlorobenzyl)-(2-phenylethyl)carbamodithioato]-(isothiocyanato)-(triphenylphosphino)-nickel(II)
E. Sathiyaraj, P. Selvaganapathi, S. Thirumaran and S. Ciattini, *J. Mol. Struct.*, 2016, **1119**, 385-395; doi: 10.1016/j.molstruc.2016.04.079
d = 3.20 Å, C–H···Cg(chelate ring) = 137° and θ = 3°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



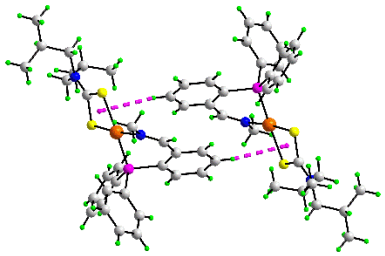
67. SUQYEI: bis(Triphenylphosphino)-[aminodiethylenebis(phthalimide)dithiocarbamate]nickel(II) perchlorate methanol solvate monohydrate
V. Venkatachalam, K. Ramalingam, G. Bocelli and A. Cantoni, *Inorg. Chim. Acta*, 1997, **257**, 49-58; doi: 10.1016/S0020-1693(96)05447-3
d = 2.80 Å, C–H···Cg(chelate ring) = 146° and θ = 10°
{About a centre of inversion, each dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



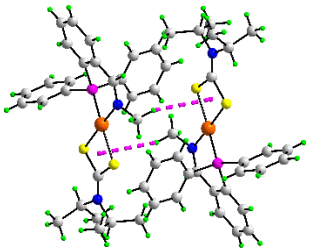
68. BAJYAN: bis(Triphenylphosphino)-(benzylisopropyldithiocarbamato)-nickel(II) perchlorate hemihydrate
R. Pastorek, J. Kameníček, J. Husárek, M. Pavlíček, Z. Šindelář, and Z. Žák, *Pol. J. Chem*., 2002, **76**, 1545-1551.
d = 2.95 Å, C–H···Cg(chelate ring) = 173° and θ = 12°
{About a centre of inversion, each dithiocarbamate ligand in the cation accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



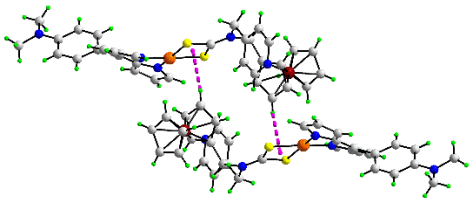
69. PACZOL: [Butane-1,4-diylbis(diphenylphosphino)]-(diallylcarbamodithioato)-nickel(II) perchlorate
K. Ramalingam, S. Srinivasan, R. Ethirajavalli and C. Rizzoli, *Polyhedron*, 2016, **104**, 138-144; doi: 10.1016/j.poly.2015.11.045
d = 2.88 Å, C–H···Cg(chelate ring) = 147° and θ = 8°
{About a centre of inversion, each dithiocarbamate ligand in the cation accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



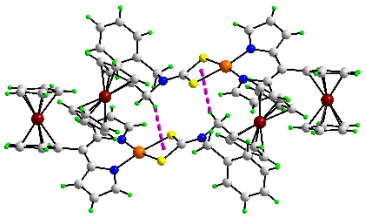
70. UMOZUR: (Di-isobutyldithiocarbamato)-(N-methyl-2-(diphenylphosphino)benzylimido)-nickel(II) perchlorate
J. L. Serrano, L. García, J. Pérez, E. Pérez, G. Sánchez, J. García, G. López, G. García and E. Molins, *Inorg. Chim. Acta*, 2003, **355**, 33-40; doi: 10.1016/S0020-1693(03)00342-6
d = 3.07 Å, C–H···Cg(chelate ring) = 164° and θ = 16°
{About a centre of inversion, each dithiocarbamate ligand in the cation accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



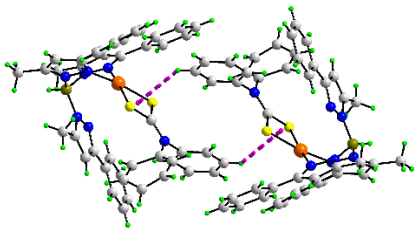
71. UMUBEJ: (Di-isopropyldithiocarbamato)-[N-methyl-2-(diphenylphosphino)benzylimido]-nickel(II) perchlorate dichloromethane solvate
J. L. Serrano, L. García, J. Pérez, E. Pérez, G. Sánchez, J. García, G. López, G. García and E. Molins, *Inorg. Chim. Acta*, 2003, **355**, 33-40; doi: 10.1016/S0020-1693(03)00342-6
d = 3.10 Å, C–H···Cg(chelate ring) = 158° and θ = 18°
{About a centre of inversion, each dithiocarbamate ligand in the cation accepts a phosphino-N-methyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



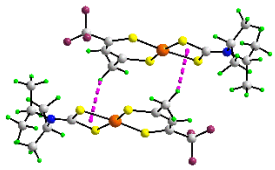
72. VOTDEP: [((1-ferrocenyl)methyl)(pyridin-4-ylmethyl)carbamodithioato]-[2-((4-(dimethylamino)-phenyl)(2H-pyrrol-2-ylidene)methyl)-1H-pyrrol-1-yl]-nickel(II)
V. Kumar, V. Singh, A. N. Gupta, S. K. Singh, M. G. B. Drew and N. Singh, *Polyhedron*, 2015, **89**, 304-312; doi: 10.1016/j.poly.2015.01.020
d = 2.94 Å, C–H···Cg(chelate ring) = 130° and θ = 13°
{About a centre of inversion, each dithiocarbamate ligand accepts a cyclopentadienyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



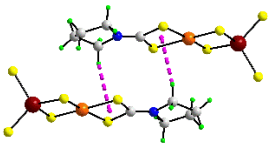
73. VIZJUL: (5-Ferrocenyl dipyrromethene)-(N-benzyl-N-ferrocenylmethyl dithiocarbamate)-nickel(II)
S. K. Singh, V. Kumar, M. G. B. Drew and N. Singh, *Inorg. Chem. Commun.*, 2013, **37**, 151-154; doi: 10.1016/j.inoche.2013.09.052
d = 3.11 Å, C–H···Cg(chelate ring) = 107° and θ = 14°
{About a centre of inversion, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



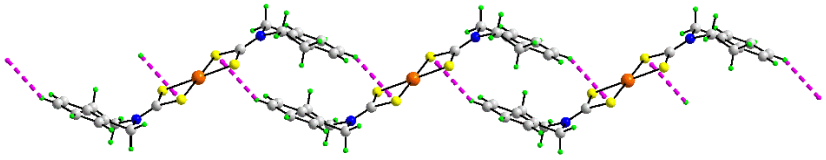
74. EGAWAL: [Hydrogen tris(3-phenyl-5-methylpyrazolyl)borate]-(diphenyldithiocarbamato)-nickel(II) acetonitrile solvate
H. Ma, S. Chattopadhyay, J. L. Petersen and M. P. Jensen, *Inorg. Chem*, 2008, **47**, 7966-7968; doi: org/10.1021/ic801099r
d = 3.24 Å, C–H···Cg(chelate ring) = 136° and θ = 15°
{About a centre of inversion, each dithiocarbamate ligand accepts a N-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



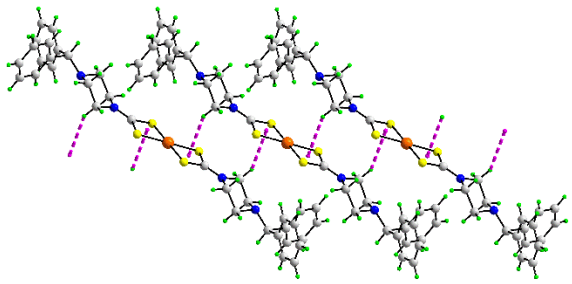
75. VARWOA: (Di-isopropyldithiocarbamato)-(1,1,1-trifluoro-2,4-pentanedithionato)-nickel(II)
I. H. Anderson, A. J. Blake and G. A. Heath, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1430-1431; doi: 10.1107/S0108270189005354
d = 2.89 Å, C–H···Cg(chelate ring) = 144° and θ = 11°
{About a centre of inversion, each dithiocarbamate ligand accepts a methyl-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



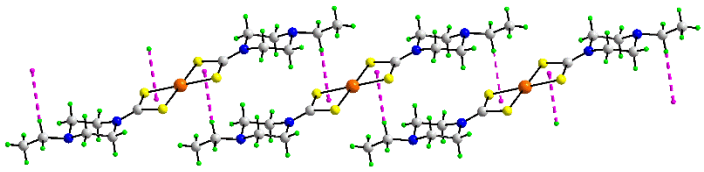
76. PELMEY: Tetraethylammonium (1-pyrrolidine-carbodithioate)-(tetrathiotungstenio)-nickel(II)
D.-L. Long, Q.-H. Wang and J.-S. Huang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 1251-1253; doi: 10.1107/S0108270198004296
d = 2.88 Å, C–H···Cg(chelate ring) = 151° and θ = 9°
{About a centre of inversion, each dithiocarbamate ligand in the cation accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular dimer}



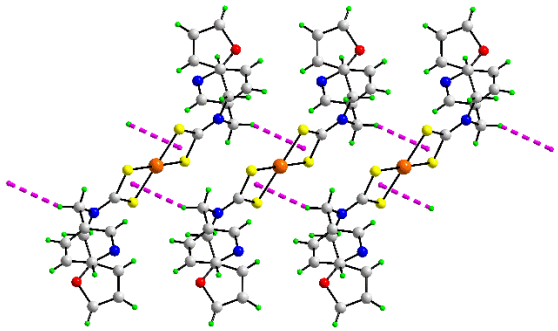
77. NAGYOL: bis(3,4-Dihydroisoquinoline-2(1H)-carbodithioato)nickel(II)
C. Anastasiadis, G. Hogarth and J. D. E. T. Wilton-Ely, *Inorg. Chim. Acta*, 2010, **363**, 3222-3228; doi: 10.1016/j.ica.2010.05.061
d = 2.85 Å, C–H···Cg(chelate ring) = 154° and θ = 12°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a phenyl-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



78. KOQPEN: bis(4-(Diphenylmethyl)piperazine-1-carbodithioato)nickel(II) chloroform solvate
B. A. Prakasam, M. Lahtinen, A. Peuronen, M. Muruganandham, E. Kolehmainen, E. Haapaniemi and M. Sillanpää, *Inorg. Chim. Acta*, 2015, **425**, 239-246; doi: 10.1016/j.ica.2014.09.016
d = 2.85 Å, C–H···Cg(chelate ring) = 150° and θ = 8°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}

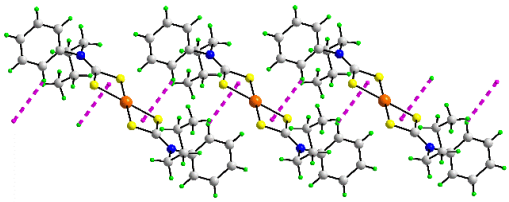


79. MEPGUK: bis(N-Ethyl-N-piperazinylcarbodithioato)nickel(II)
Y. Wang and L.-H. Yan, *Chin. J. Struct. Chem*., 2006, **25**, 1260-1264.
d = 2.86 Å, C–H···Cg(chelate ring) = 176° and θ = 18°
{Centrosymmetric molecules self-associate by accepting and donating two N-methylene-C–H···Cg(chelate ring) interactions on either side of the square-plane to form supramolecular chain with a linear topology}

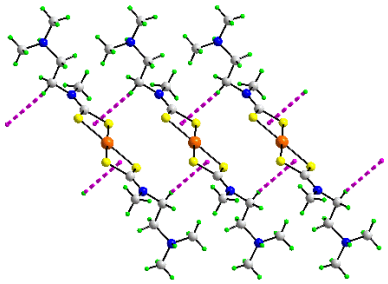


80. DIFHIL: bis[(2-Furylmethyl)(pyridin-3-ylmethyl)carbamodithioato]nickel(II)
G. Rajput, V. Singh, A. N. Gupta, M. K. Yadav, V. Kumar, S. K. Singh, A. Prasad, M. G. B. Drew and N. Singh, *CrystEngComm*, 2013, **15**, 4676-4683; doi: 10.1039/c3ce27096c
d = 2.91 Å, C–H···Cg(chelate ring) = 156° and θ = 18°

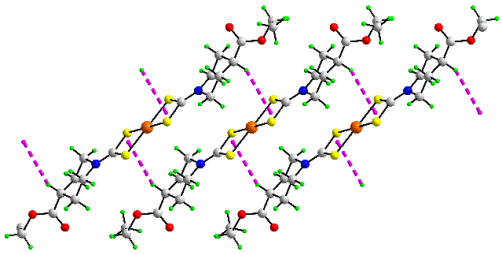
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



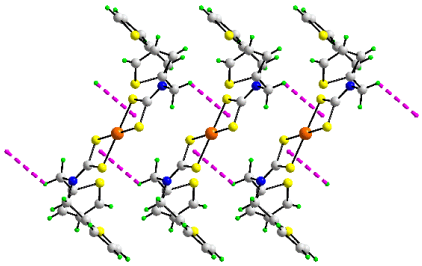
81. OBAKAG: bis(N-Butyl-N-phenyl dithiocarbamato)nickel(II)
D. C. Onwudiwe, A. C. Ekennia and E. Hosten, *J. Coord. Chem.*, 2016, **69**, 2454-2468; doi: 10.1080/00958972.2016.1186800
d = 3.00 Å, C–H···Cg(chelate ring) = 137° and θ = 17°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a methyl-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



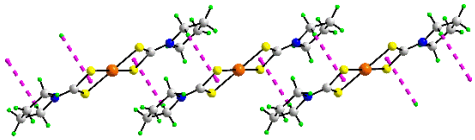
82. OJERAY: bis[(2-(Dimethylaminio)ethyl)methylcarbamodithioato]nickel(II) dichloride
W. Clegg and R. A. Coxall, *Private Communication to the Cambridge Structural Database*, 2016, Refcode OJERAY.
d = 3.05 Å, C–H···Cg(chelate ring) = 115° and θ = 8°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



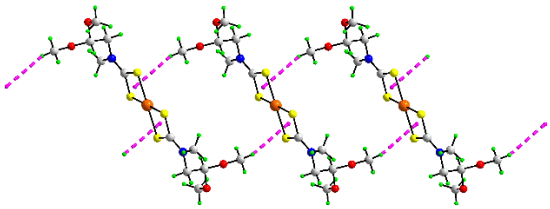
83. HOMWOX: bis[4-(Ethoxycarbonyl)piperidine-1-dithiocarboxylato]nickel(II)
A. N. Gupta, V. Kumar, V. Singh, K. K. Manar, M. G. B. Drew and N. Singh, *CrystEngComm*, 2014, **16**, 9299-9307; doi: 10.1039/C4CE01263A
d = 3.14 Å, C–H···Cg(chelate ring) = 155° and θ = 13°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a methine-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



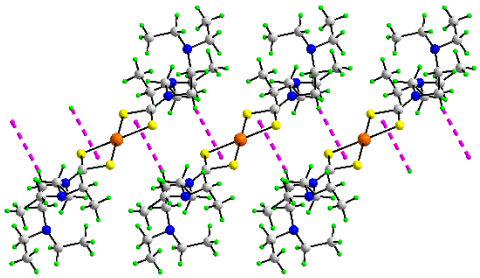
84. GIGWIC: bis(bis(2-Thienylmethyl)dithiocarbamato)nickel(II)
Ya. L. Gol'dfarb, E. G. Ostapenko, V. G. Vinogradova, A. N. Zverev, A. V. Polyakov, A. I. Yanovsky, D. S. Yufit and Yu. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 1987, pp. 902-909.
d = 3.15 Å, C–H···Cg(chelate ring) = 117° and θ = 8°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



85. PYRCTN01: bis(Tetrahydropyrrole-1-carbodithioato)nickel(II)
L. M. Engelhardt, J. M. Patrick and A. H. White, *Aust. J. Chem.*, 1985, **38**, 1413-1416; doi: 10.1071/CH9851413
d = 3.18 Å, C–H···Cg(chelate ring) = 121° and θ = 18°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}

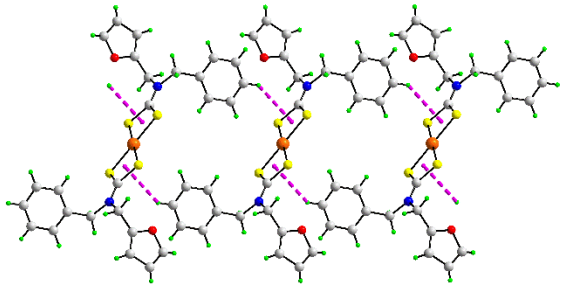


86. FUHXAJ: bis[(2,2-Dimethoxyethyl)methylcarbamodithioato]nickel(II)
I. P. Ferreira, G. M. de Lima, E. B. Paniago, J. A. Takahashi and C. B. Pinheiro, *Inorg. Chim Acta*, 2014, **423A**, 443-449; doi: 10.1016/j.ica.2014.09.002
d = 3.18 Å, C–H···Cg(chelate ring) = 123° and θ = 15°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts an O-methyl-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}

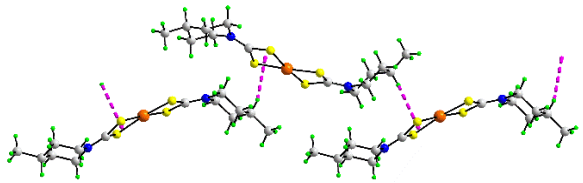


87. QOWXEG: bis[bis(2-(Diethylamino)ethyl)carbamodithioato]nickel(II)

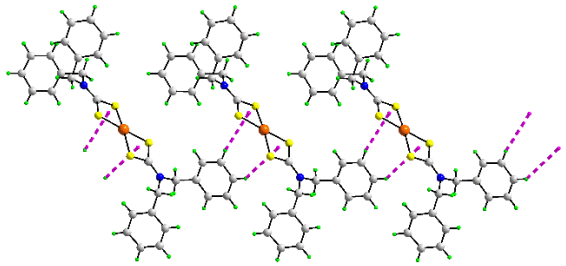
G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent, S. E. Kabir, I. Richards and J. D. E. T. Wilton-Ely and Q. Zhang, *Inorg. Chim Acta*, 2009, **362**, 2020-2026; doi: 10.1016/j.ica.2008.09.030
d = 3.19 Å, C–H···Cg(chelate ring) = 132° and θ = 17°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



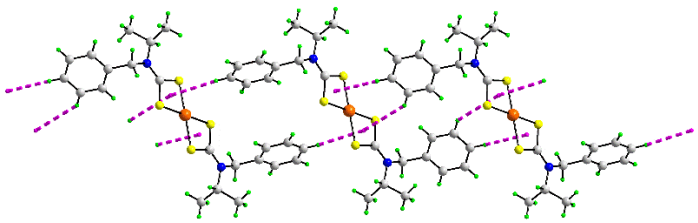
88. DIDTIV01: bis(Benzyl(2-furylmethyl)carbamodithioato)nickel(II)
P. Valarmathi, S. Thirumaran, L. Sarmal and R. Kant, *Spectrochim. Acta, Part A*, 2014, **129**, 285-292; doi: 10.1016/j.saa.2014.03.068
d = 3.27 Å, C–H···Cg(chelate ring) = 143° and θ = 12°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts a phenyl-C–H···Cg(chelate ring) interaction on either side of the square-plane to form supramolecular chain with a linear topology}



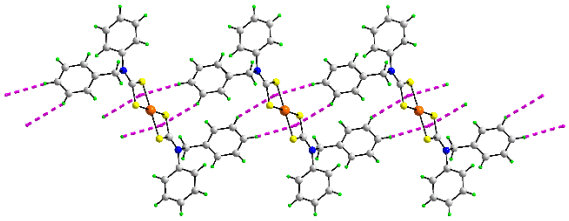
89. YUGLOC: bis(4-Methylpiperidine-1-carbodithioato)nickel(II)
N. Srinivasan, V. Sathyaselvabala, K. Kuppulekshmy, P. Valarmathi and S. Thirumaran, *Monatsh. Chem. Acta*, 2009, **140**, article no. 1431; doi: 10.1007/s00706-009-0199-2
d = 3.13 Å, C–H···Cg(chelate ring) = 154° and θ = 16°
{One dithiocarbamate ligand accepts a methine-C–H···Cg(chelate ring) interaction to form supramolecular chain with a helical (2_1) topology}



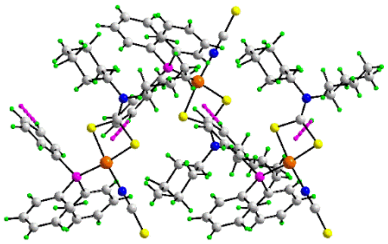
90. MAXGOI: bis(Dibenzyldithiocarbamato)-triiodidostibine-nickel(II) carbon disulfide solvate
R. Pastorek, J. Kameníček, Z. Trávníček, M. Pavlíček, B. Cvek, J. Husárek and Z. Šindelar, *Pol. J. Chem.*, 2005, **79**, 637-644.
d = 3.07 Å, C–H···Cg(chelate ring) = 162° and θ = 17°
d = 3.16 Å, C–H···Cg(chelate ring) = 141° and θ = 14°
{In the molecule, each dithiocarbamate ligand accepts a phenyl-C–H···Cg(chelate ring) interaction and a supramolecular chain ensues, with a linear topology. In essence, translationally related molecules are connected by bridging phenyl rings employing two H atoms}



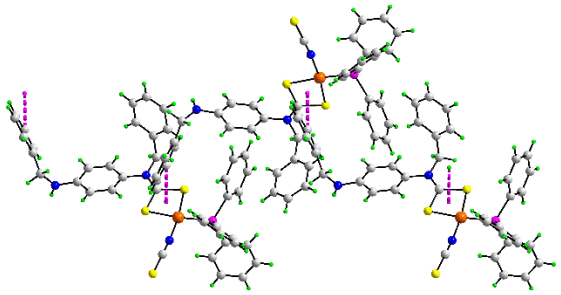
91. TADKAN: bis[Benzyl(isopropyl)carbamodithioato]nickel(II)
J. Masnovi, N. V. Duffy, P. E. Fanwick and A. F. Hepp, *J. Coord. Chem.*, 2016, **69**, 90-102; doi: 10.1080/00958972.2015.1107904
d = 2.91 Å, C–H···Cg(chelate ring) = 166° and θ = 14°
d = 3.16 Å, C–H···Cg(chelate ring) = 163° and θ = 16°
d = 3.24 Å, C–H···Cg(chelate ring) = 143° and θ = 15°
{In the molecule, each dithiocarbamate ligand accepts a N-bound phenyl-C–H···Cg(chelate ring) interaction whereby a bridging phenyl rings employing two H atoms to provide the links. One of the dithiocarbamate ligands also forms a second N-bound phenyl-C–H···Cg(chelate ring) interaction; this dithiocarbamate ligand forms the longer of the *d* separations. The result is a twisted ($\bar{1}$) supramolecular chain}



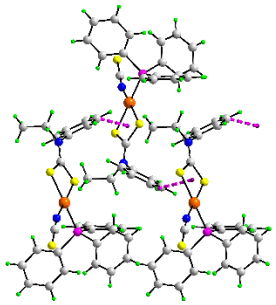
92. TADKIV: bis[Benzyl(phenyl)carbamodithioato]nickel(II)
J. Masnovi, N. V. Duffy, P. E. Fanwick and A. F. Hepp, *J. Coord. Chem.*, 2016, **69**, 90-102; doi: 10.1080/00958972.2015.1107904
d = 3.05 Å, C–H···Cg(chelate ring) = 164° and θ = 13°
d = 3.24 Å, C–H···Cg(chelate ring) = 148° and θ = 13°
{In the centrosymmetric molecule, each dithiocarbamate ligand accepts four N-bound phenyl-C–H···Cg(chelate ring) interactions provided by two bridging phenyl rings employing two H atoms each. The result is a linear supramolecular chain}



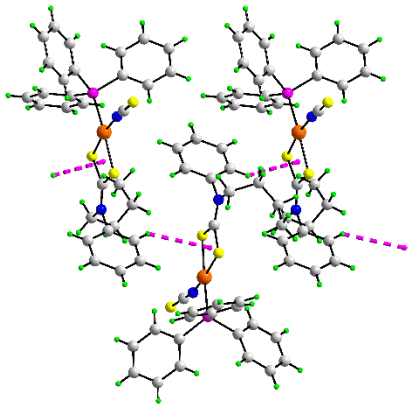
93. PEDYON: (Dicyclohexyldithiocarbamato)-(isothiocyanato)-(triphenylphosphino)-nickel(II)
B. A. Prakasam, K. Ramalingam, G. Bocelli and A. Cantoni, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 113-117; doi: 10.1246/bcsj.79.113
d = 2.90 Å, C–H···Cg(chelate ring) = 170° and θ = 6°
{The dithiocarbamate ligand accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



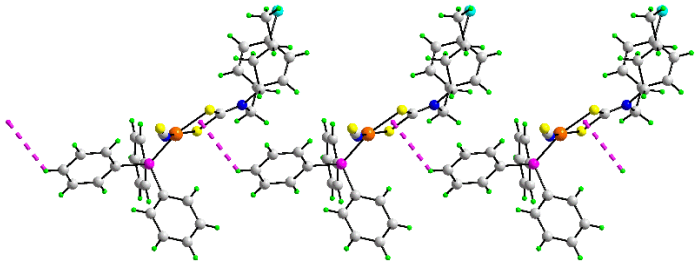
94. SUKWAY: [Benzyl(4-(benzylamino)phenyl)dithiocarbamate]-isothiocyanato-triphenylphosphino-nickel(II)
E. Sathiyaraj, P. Valarmathi, S. Thirumaran, S. Ciattini, V. K. Gupta and R. Kant, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 2015, **190**, 1127-1137; doi: 10.1080/10426507.2014.976337
d = 2.98 Å, C–H···Cg(chelate ring) = 143° and θ = 12°
{The dithiocarbamate ligand accepts a N-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a zig-zag (glide) topology}



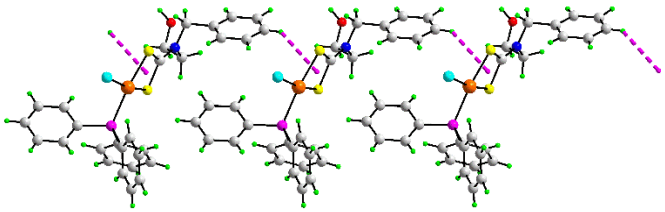
95. ZAKBEV: (N-Ethyl-N-phenyl dithiocarbamato)-isothiocyanato-triphenylphosphino-nickel(II)
D. C. Onwudiwe, M. M. Kabanda, E. E. Ebenso and E. C. Hosten, *J. Chem. Sci. (Bangalore, India)*, 2016, **128**, 1081-1093; doi: 10.1007/s12039-016-1111-3
d = 2.99 Å, C–H···Cg(chelate ring) = 143° and θ = 10°
{The dithiocarbamate ligand accepts a N-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



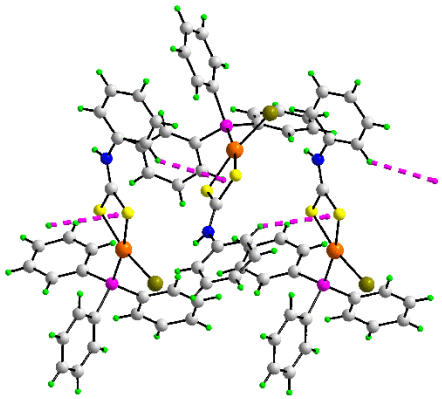
96. OBAJUZ: (N-butyl-N-phenyl dithiocarbamato)-(isothiocyanato)-(triphenylphosphino)-nickel(II)
D. C. Onwudiwe, A. C. Ekennia and E. Hosten, *J. Coord. Chem.*, 2016, **69**, 2454-2468; doi: 10.1080/00958972.2016.1186800
d = 3.15 Å, C–H···Cg(chelate ring) = 132° and θ = 16°
{The dithiocarbamate ligand accepts a N-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



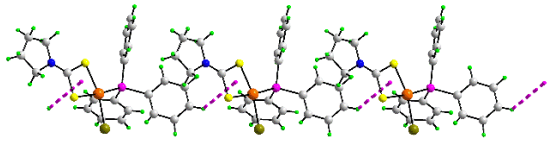
97. KOQTUH: (Butyl(4-chlorobenzyl)carbamodithioato)-thiocyanato-triphenylphosphino-nickel(II)
B. A. Prakasam, M. Lahtinen, A. Peuronen, M. Muruganandham, E. Kolehmainen, E. Haapaniemi and M. Sillanpää, *Inorg. Chim. Acta*, 2015, **425**, 239-246; doi: 10.1016/j.ica.2014.09.016
d = 3.19 Å, C–H···Cg(chelate ring) = 120° and θ = 10°
{The dithiocarbamate ligand accepts a phosphino-bound C–H···Cg(chelate ring) interaction to form a supramolecular chain with a linear topology}



98. QOXKAQ: [N-Benzyl-N-(2-hydroxyethyl)carbamodithioato]-(chlorido)-(triphenylphosphino)-nickel(II)
R. Baskaran, K. Ramalingam, R. Thiruneelakandan, B. A. Prakasam, G. Bocelli and A. Cantoni, *J. Coord. Chem.*, 2009, **62**, 1076-1085; doi: 10.1080/00958970802483624
d = 3.16 Å, C–H···Cg(chelate ring) = 140° and θ = 17°
{The dithiocarbamate ligand accepts a phosphino-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a linear topology}



99. GEGLEK: Bromido-triphenylphosphino-(N-phenyldithiocarbamato)-nickel(II) chloroform solvate
R. Pastorek, J. Kameníček, H. Vrbová, V. Slovák and M. Pavlíček, *J. Coord. Chem.*, 2006, **59**, 437-444; doi: 10.1080/00958970500490798
d = 2.95 Å, C–H···Cg(chelate ring) = 141° and θ = 17°
{The dithiocarbamate ligand accepts a N-bound phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a zig-zag (glide) topology. Intermolecular dithiocarbamate-N–H···Br hydrogen bonding (2.60 Å) is noted within the chain}

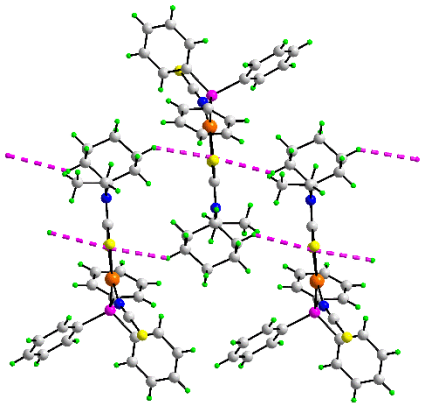


100. TIZJAN: Bromido-(pyrrolidinedithiocarbamato)-triphenylphosphino-nickel(II) chloroform solvate

R. Pastorek, Z. Trávníček, Z. Šindelář, F. Březina and J. Marek, *Polyhedron*, 1996, **15**, 3691-3695; doi: 10.1016/0277-5387(96)00126-X

d = 2.99 Å, C–H···Cg(chelate ring) = 152° and θ = 9°

{The dithiocarbamate ligand accepts a phosphino-bound C–H···Cg(chelate ring) interaction to form a supramolecular chain with a linear topology}



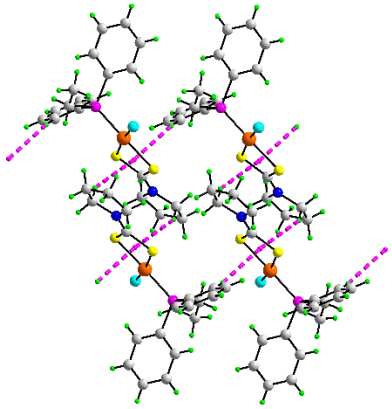
101. FAJRUF: [Cyclohexyl(ethyl)carbamodithioato]-(thiocyanato)-(triphenylphosphino)-nickel(II)

S. Srinivasan, K. Ramalingam and C. Rizzoli, *Polyhedron*, 2012, **33**, 60-66; doi: 10.1016/j.poly.2011.11.027

d = 3.03 Å, C–H···Cg(chelate ring) = 142° and θ = 19°

d = 3.30 Å, C–H···Cg(chelate ring) = 126° and θ = 7°

{One of the two independent molecules self-associates *via* methylene-C–H···Cg(chelate ring) interactions on both sides of the dithiocarbamate to form a supramolecular chain with a twisted ($\bar{1}$) topology}



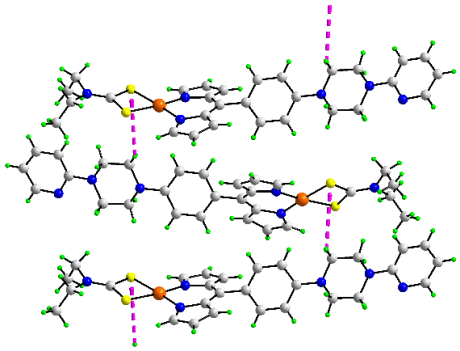
102. LOBRIE: Chlorido-(ethyldiphenylphosphino)-(1-pyrrolidinecarbodithioato)-nickel(II)

A. Kropidlowska, I. Turowska-Tyrk and B. Becker, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, **64**, m748; doi: 10.1107/S1600536808011860

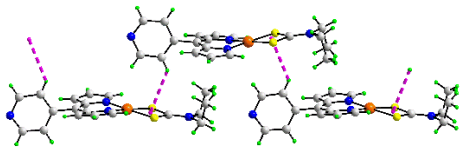
d = 2.83 Å, C–H···Cg(chelate ring) = 148° and θ = 4°

d = 3.06 Å, C–H···Cg(chelate ring) = 147° and θ = 14°

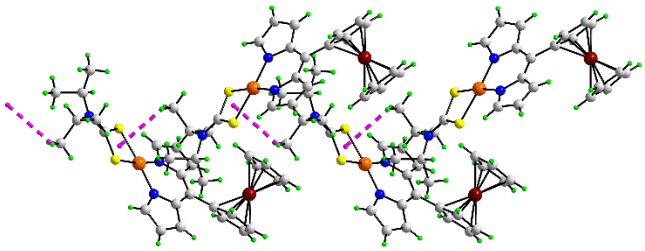
{The molecules self-associate *via* phenyl-C–H···Cg(chelate ring) (first entry) and N-methylene-C–H···Cg(chelate ring) interactions on both sides of the dithiocarbamate ligand to form a supramolecular chain with a twisted ($\bar{1}$) topology}



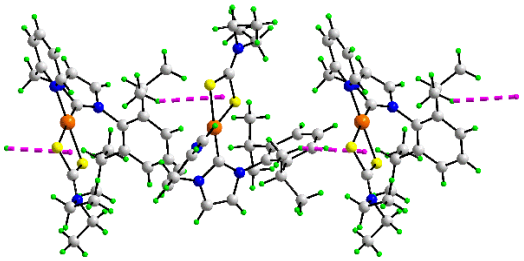
103. EKUQEI: (Diethylcarbamodithioato)-[1-(pyridin-2-yl)-4-(4-((1H-pyrrol-2-yl)(2H-pyrrol-2-ylidene)methyl)phenyl)piperazinato]-nickel(II)
R. K. Gupta, V. Kumar, A. Srivastava and D. S. Pandey, *RSC Advances*, 2016, **6**, 40911-40915; doi: 10.1039/C6RA03835B
d = 3.09 Å, C–H···Cg(chelate ring) = 126° and θ = 20°
{The dithiocarbamate ligand accepts a N-methylene-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



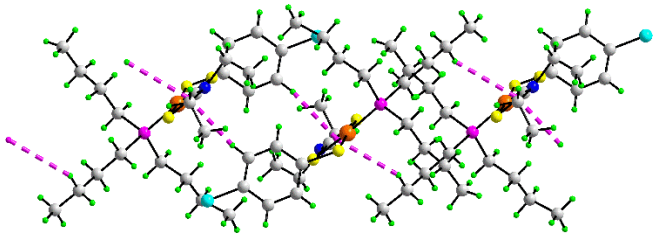
104. ZOYYAP: (Diethylcarbamodithioato)-[4-((1H-pyrrol-2-yl)(2H-pyrrol-2-ylidene)methyl)-pyridinato]-nickel(II)
R. K. Gupta, M. Dubey, P. Zhou Li, Q. Xu and D. S. Pandey, *Inorg. Chem.*, 2015, **54**, 2500-2511; doi: 10.1021/ic502848a
d = 3.12 Å, C–H···Cg(chelate ring) = 128° and θ = 16°
{There are two independent molecules in the asymmetric unit. One of these self-assembles as the dithiocarbamate ligand accepts a pyridyl-C–H···Cg(chelate ring) interaction. The result is a supramolecular chain with a helical (2_1) topology}



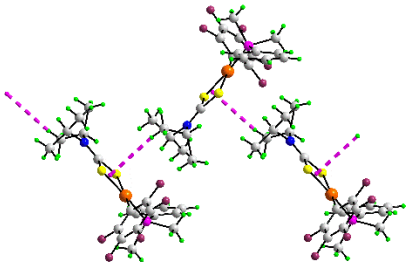
105. YEFVIQ: (5-Ferrocenyldipyrromethene)-(di-isopropyldithiocarbamate)-nickel(II)
R. K. Gupta, R. Pandey, R. Singh, N. Srivastava, B. Maiti, S. Saha, P. Li, Q. Xu and D. S. Pandey, *Inorg. Chem.*, 2012, **51**, 8916-8930; doi: 10.1021/ic300900m
d = 3.26 Å, C–H···Cg(chelate ring) = 118° and θ = 19°
{The dithiocarbamate ligand accepts and donates a methyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



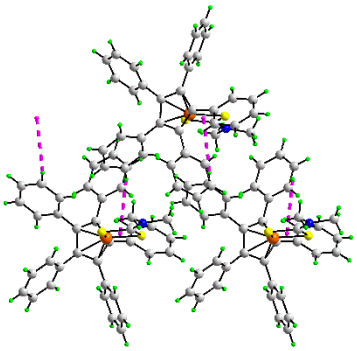
106. FEGXEV: [1-(2,6-Diisopropylphenyl)-3-(a-picolyl)imidazol-2-ylidene]-(diethyldithiocarbamato)-nickel(II) bromide dichloromethane solvate
S. Winston, N. Stylianides, A. A. D. Tulloch, J. A. Wright and A. A. Danopoulos, *Polyhedron*, 2014, **23**, 2813-2820; doi: 10.1016/j.poly.2004.07.002
d = 3.21 Å, C–H···Cg(chelate ring) = 153° and θ = 17°
{The dithiocarbamate ligand accepts a methyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



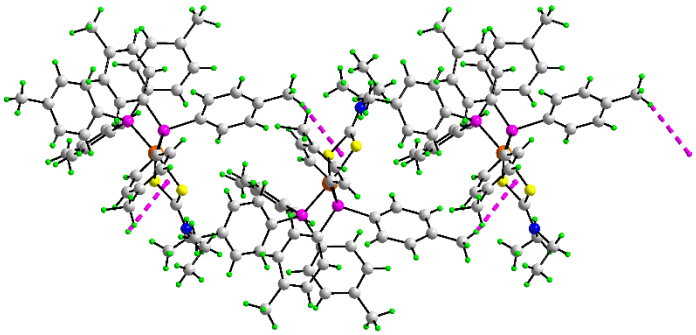
107. LERSIK: (Diethyldithiocarbamato)-(4-chlorophenylthiolato)-(tri-n-butylphosphino)-nickel(II)
J. Darkwa, E. Y. Osei-Twum and L. A. Litorja Jr, *Polyhedron*, 1999, **18**, 1115-1122; doi: 10.1016/S0277-5387(98)00400-8
d = 2.88 Å, C–H···Cg(chelate ring) = 167° and θ = 7°
d = 3.21 Å, C–H···Cg(chelate ring) = 139° and θ = 19°
{The molecules self-associates *via* phenyl-C–H···Cg(chelate ring) (first entry) and methylene-C–H···Cg(chelate ring) interactions on both sides of the dithiocarbamate to form a supramolecular chain with a twisted ($\bar{1}$) topology}



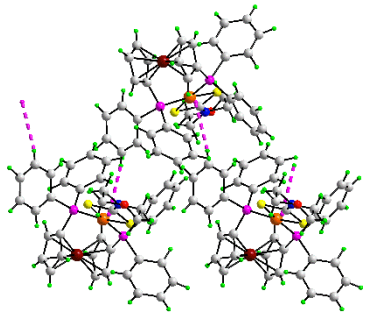
108. XAJWOU: (Di-isopropyldithiocarbamato)-(dimethylphenylphosphino)-(perfluorophenyl)-nickel(II)
G. Sánchez, F. Ruíz, J. L. Serrano, M. C. Ramírez de Arellano and G. López, *Eur. J. Inorg. Chem.*, 2000, pp. 2185-2191; doi: 10.1002/1099-0682(200010)2000:10<2185::AID-EJIC2185>3.0.CO;2-K
d = 3.26 Å, C–H···Cg(chelate ring) = 162° and θ = 4°
{The dithiocarbamate ligand accepts a dithiocarbamate-bound methyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



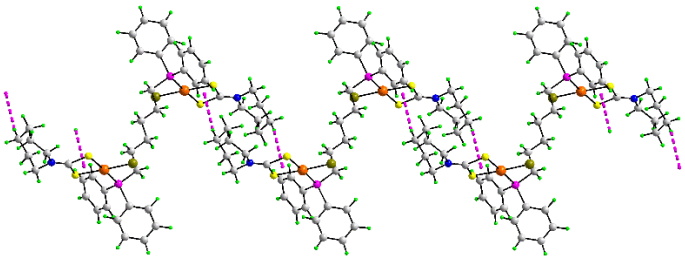
109. KIDLAK: (η^5-Pentaphenyl-cyclopentadienyl)-(dimethyldithiocarbamato)-nickel tetrafluoroborate
M. Huhn, W. Kläui, L. Ramacher, R. Herbst-Irmer and E. Egert, *J. Organomet. Chem.*, 1990, **398**, 339-350; doi: 10.1016/0022-328X(90)85519-5
d = 3.24 Å, C–H···Cg(chelate ring) = 137° and θ = 18°
{The dithiocarbamate ligand accepts a phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}



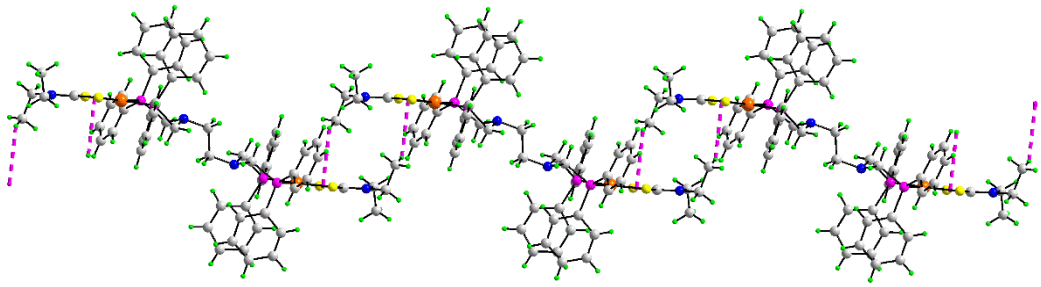
110. FAVZEI: (Diethyldithiocarbamato)-bis[tris(4-tolyl)phosphino]-nickel(II) perchlorate
R. Thiruneelakandan, K. Ramalingam, G. Bocelli and L. Righi, *Z. Anorg. Allg. Chem.*, 2015, **631**, 187-193; doi: 10.1002/zaac.200400245
d = 3.23 Å, C–H···Cg(chelate ring) = 138° and θ = 18°
{The dithiocarbamate ligand accepts a methyl-C–H···Cg(chelate ring) interaction to form supramolecular chain with a zig-zag (glide) topology}



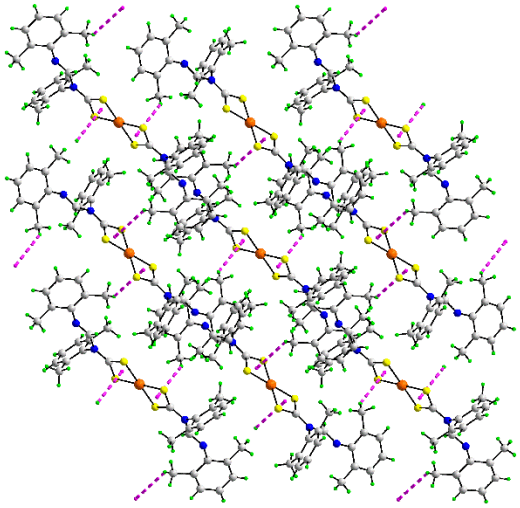
111. QIDRAW: (Morpholinedithiocarbamate)-(1,1'-bis(diphenylphosphino)ferrocene)-nickel(II) perchlorate ethanol solvate
R. Pastorek, J. Kameníček, Z. Šindelář and Z. Žák, *Pol. J. Chem.*, 2001, **75**, 363-369.
d = 3.03 Å, C–H···Cg(chelate ring) = 159° and θ = 10°
{The dithiocarbamate ligand in the cation accepts a phosphino-phenyl-C–H···Cg(chelate ring) interaction to form a supramolecular chain with a helical (2_1) topology}

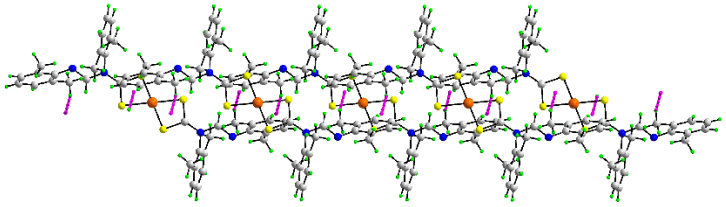


112. EJIXAW: [μ2-1,6-bis(Diphenylphosphino)hexane]-bis(hexamethyleneiminedithiocarbamato)-dibromo-di-nickel(II) chloroform solvate
R. Pastorek, J. Kameniček, J. Husárek, M. Pavlíček, Z. Šindelář, and Z. Žák, *Pol. J. Chem.*, 2003, **77**, 805-812.
d = 3.16 Å, C–H···Cg(chelate ring) = 162° and θ = 10°
{In the centrosymmetric, binuclear molecule, each dithiocarbamate ligand accepts a methylene-C–H···Cg(chelate ring) interaction and a supramolecular chain ensues, with a zig-zag (glide) topology}

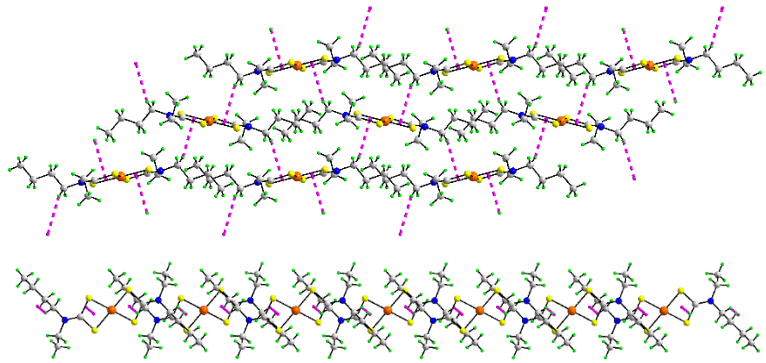


113. HILWUW: (μ-tetrakis[(Diphenylphosphino)methyl]ethane-1,2-diamine)-bis(diethylcarbamo-dithioato)-di-nickel(II) bis(hexafluorophosphate) hexane solvate
X.-Y. Wu, Z.-G. Ren and J.-P. Lang, *Dalton Trans.*, 2014, **43**, 1716-1723; doi: 10.1039/C3DT52412D
d = 3.19 Å, C–H···Cg(chelate ring) = 115° and θ = 4°
{In the centrosymmetric, binuclear molecule, each dithiocarbamate ligand accepts a methyl-C–H···Cg(chelate ring) interaction and a supramolecular chain ensues, with a twisted topology}

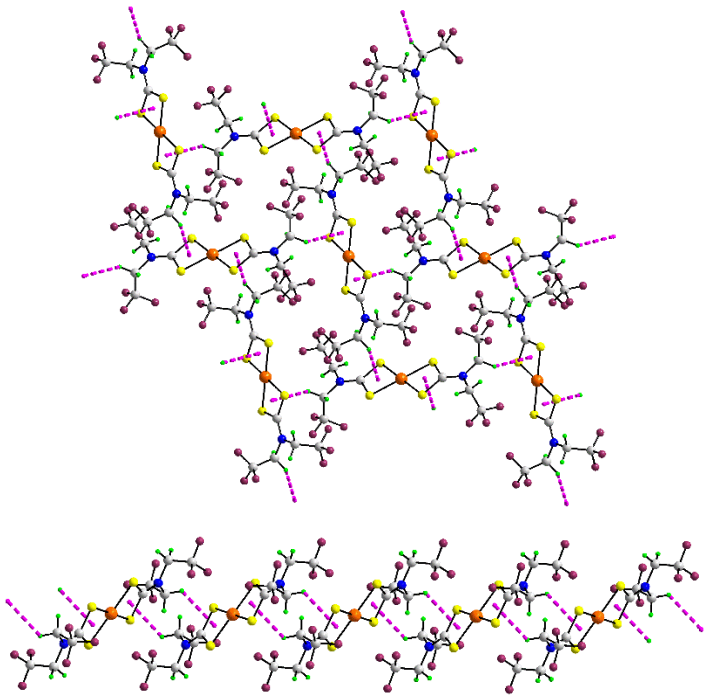




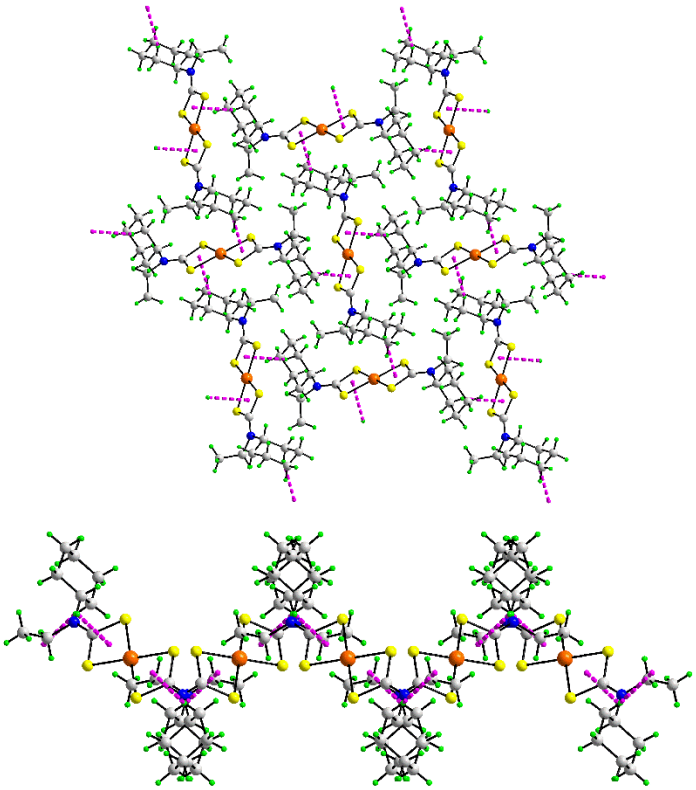
114. LONKIL: bis[(2,6-Dimethylphenyl){[(2,6-dimethylphenyl)imino]methyl}-carbamodithioato)]nickel(II)
S. D. Oladipo, B. Omondi and C. Mocktar, *Polyhedron*, 2019, **170**, 712-722; doi: 10.1016/j.poly.2019.06.038
d = 3.01 Å, C–H···Cg(chelate ring) = 134° and θ = 3°
{Each centrosymmetric molecule accepts and donates two methyl-C–H···Cg(chelate ring) interactions. These interactions extend laterally to form a square grid – note the parallel arrangement of molecules}



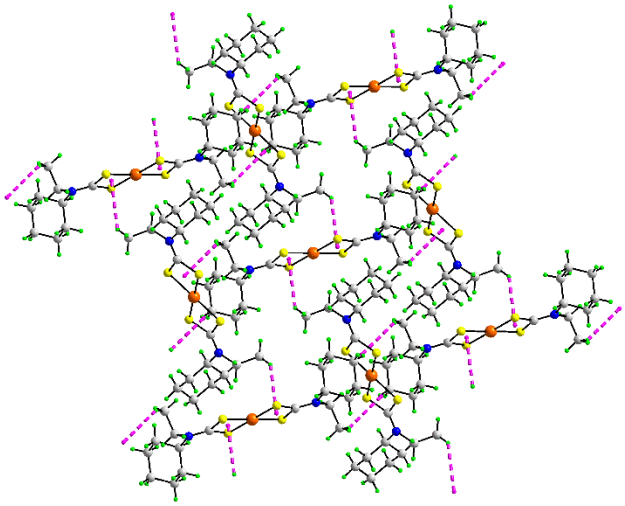
115. PUHVIY01: bis[Butyl(ethyl)carbamodithioato]nickel(II)
J. Masnovi, N. V. Duffy, P. E. Fanwick and A. F. Hepp, *J. Coord. Chem.*, 2016, **69**, 90-102; doi: 10.1080/00958972.2015.1107904
d = 3.04 Å, C–H···Cg(chelate ring) = 129° and θ = 5°
{Each centrosymmetric molecule accepts and donates two N-butyl-methylene-C–H···Cg(chelate ring) interactions. These interactions extend laterally to form a 2-D array – note the parallel alignment of horizontal rows but, these are off-set}

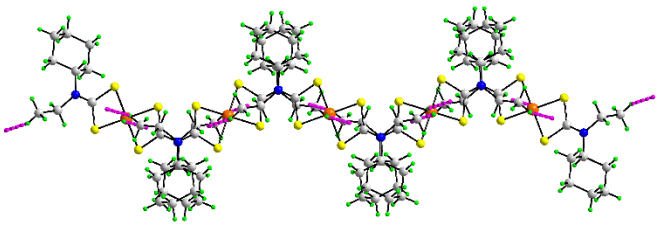


116. FIDGEE: bis[bis(Trifluoroethyl)dithiocarbamate]nickel(II)
M. R. Sundberg and M.-L. Riekkola, *Inorg. Chim. Acta*, 1987, **99**, 99-103; doi: 10.1016/S0020-1693(00)83997-3
d = 3.07 Å, C–H···Cg(chelate ring) = 126° and θ = 12°
{Centrosymmetric molecule. Accepts and donates two N-methylene-C–H···Cg(chelate ring) interactions, extending laterally, to form a 2-D array}

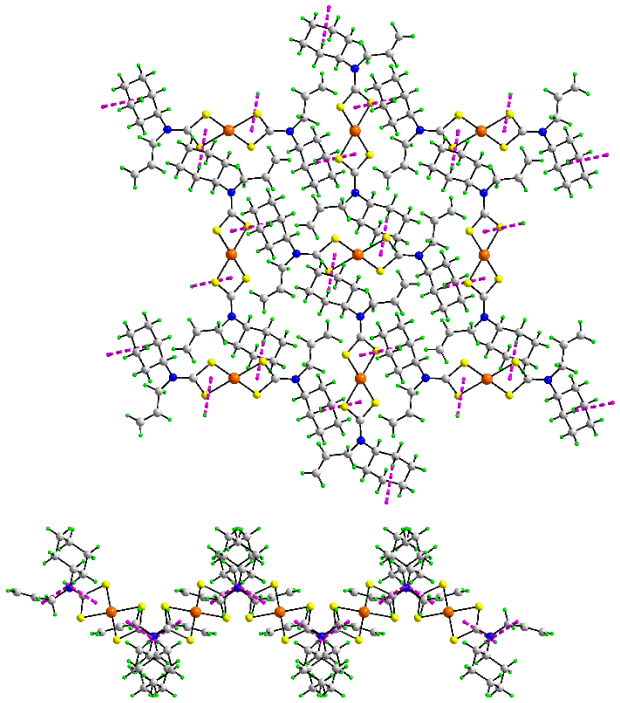


117. GOQYAM: bis(N-Cyclohexyl-N-ethyldithiocarbamato)nickel(II) – polymorph I
S. Srinivasan, K. Ramalingam and C. Rizzoli, *Polyhedron*, 2012, **33**, 60-66; doi: 10.1016/j.poly.2011.11.027
d = 2.91 Å, C–H···Cg(chelate ring) = 160° and θ = 7°
{Centrosymmetric molecule. Accepts and donates two methyl-C–H···Cg(chelate ring) interactions, extending laterally, to form a 2-D array}

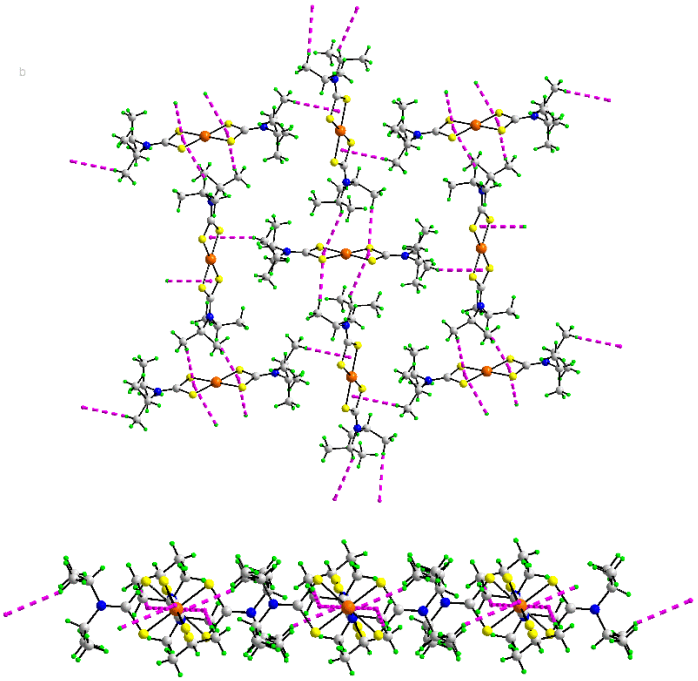




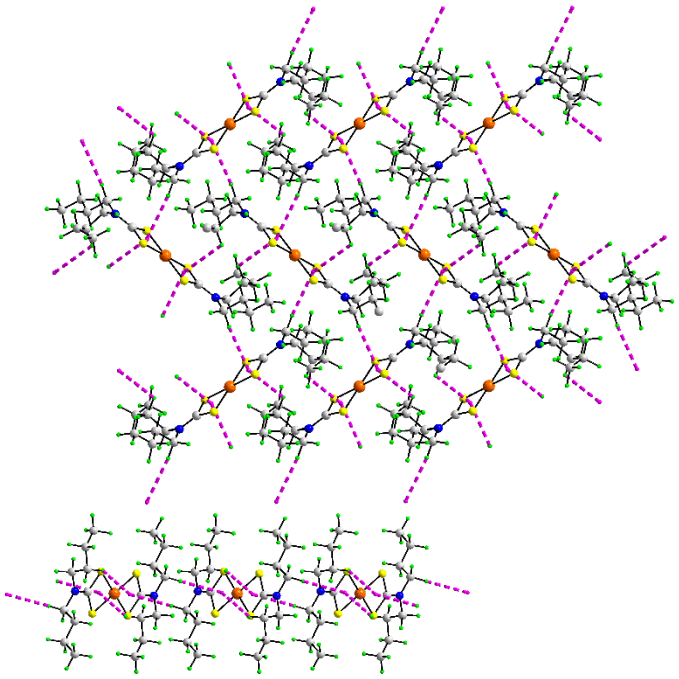
118. GOQYAM: bis(N-Cyclohexyl-N-ethyldithiocarbamato)nickel(II) – polymorph II
M. J. Cox and E. R. T. Tiekink, *Z. Kristallogr*., 1999, **119**, 242-250; doi: 10.1524/zkri.1999.214.4.242
d = 3.07 Å, C–H···Cg(chelate ring) = 135° and θ = 8°
{Centrosymmetric molecule. Accepts and donates two methyl-C–H···Cg(chelate ring) interactions, extending laterally, to form a 2-D array}



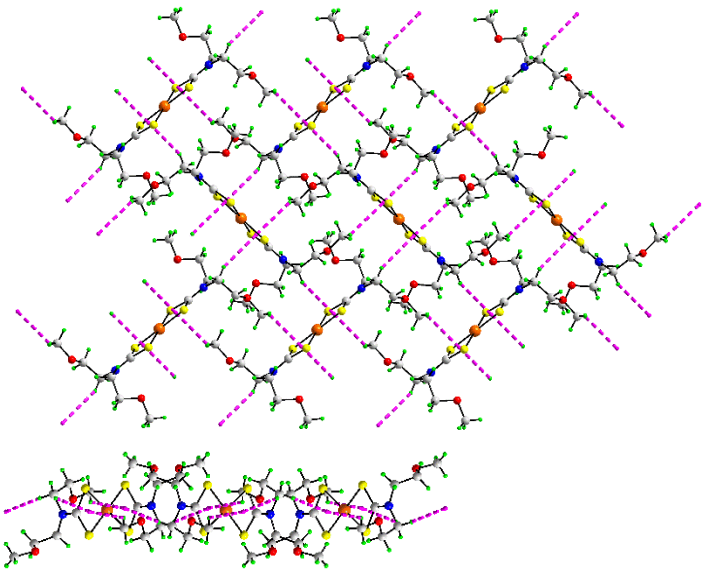
119. BEMHIM: bis(Allyl(cyclohexyl)carbamodithioato)nickel(II)
S. Srinivasan, K. Ramalingam and C. Rizzoli, *Z. Anorg. Allg. Chem*., 2012, **638**, 1356-1361; doi: 10.1002/zaac.201200103
d = 3.13 Å, C–H···Cg(chelate ring) = 170° and θ = 18°
{Centrosymmetric molecule. Accepts and donates two methylene-C–H···Cg(chelate ring) interactions, extending laterally, to form a 2-D array}



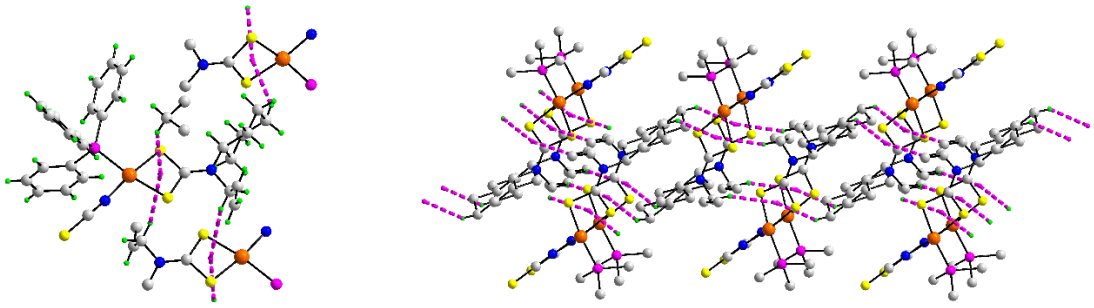
120. IPTCNI10: bis(Di-isopropyldithiocarbamato)nickel(II)
P. C. Healy, J. W. Connor, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1990, **43**, 1083-1095; doi: 10.1071/CH9901083
d = 3.17 Å, C–H···Cg(chelate ring) = 158° and θ = 6°
d = 3.17 Å, C–H···Cg(chelate ring) = 161° and θ = 13°
d = 3.22 Å, C–H···Cg(chelate ring) = 139° and θ = 20°
{There are two centrosymmetric molecules comprising the asymmetric unit. One accepts and donates two methyl-C–H···Cg(chelate ring) interactions (first entry). The other accepts and donates pairs of methyl-C–H···Cg(chelate ring) and methine-C–H···Cg(chelate ring) interactions (second and third listings, respectively). These interactions extend laterally to form a 2-D array. Missing hydrogen atom included employing *Mercury*}

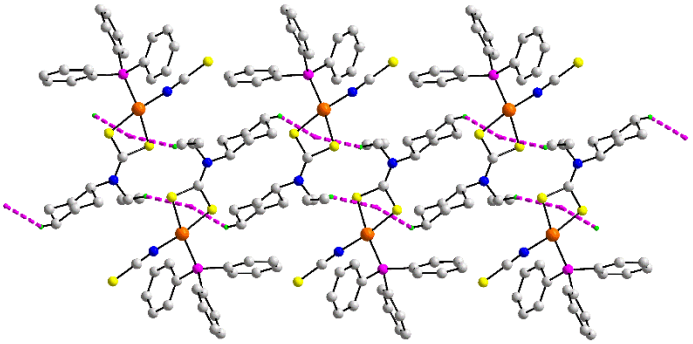


121. CIYSEI: bis(Dibutylcarbamodithioato)-nickel(II)
J. Lokaj, V. Vrabel and E. Kellö, *Chem. Zvesti*, 1984, **38**, 313-320.
d = 3.06 Å, C–H···Cg(chelate ring) = 174° and θ = 16°
d = 3.20 Å, C–H···Cg(chelate ring) = 108° and θ = 17°
{Centrosymmetric molecule. Accepts and donates two N-methylene-C–H···Cg(chelate ring) interactions, extending laterally, to form a 2-D array. There are also methylene-C–H···Cg(chelate ring) interactions (second entry) just outside the search criteria reinforcing the supramolecular assembly}

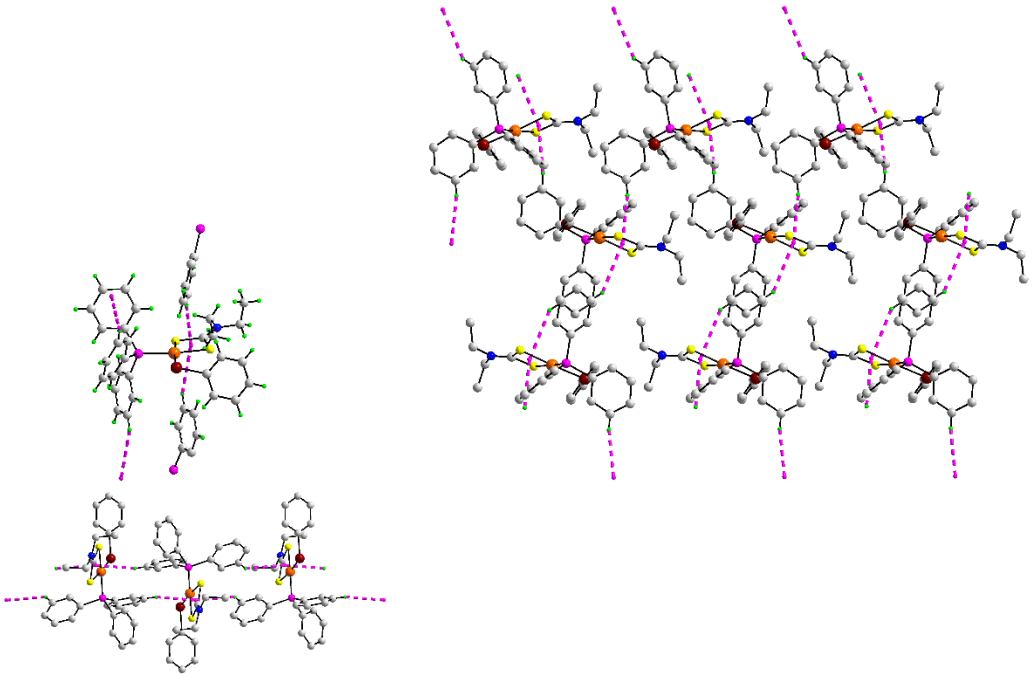


122. SOTNOF: bis[bis(2-Methoxyethyl)carbamodithioato]nickel(II)
G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent and I. Richards, *Inorg. Chim. Acta*, 2009, **362**, 1361-1364; doi: 10.1016/j.ica.2008.05.010
d = 3.11 Å, C–H···Cg(chelate ring) = 131° and θ = 10°
d = 3.24 Å, C–H···Cg(chelate ring) = 158° and θ = 18°
{Centrosymmetric molecule. Each accepts and donates and two methoxy-C–H···Cg(chelate ring), first listing, and two N-methylene-C–H···Cg(chelate ring) interactions, extending laterally, to form a 2-D array. A side-on view suggests some corrugation in the layer}

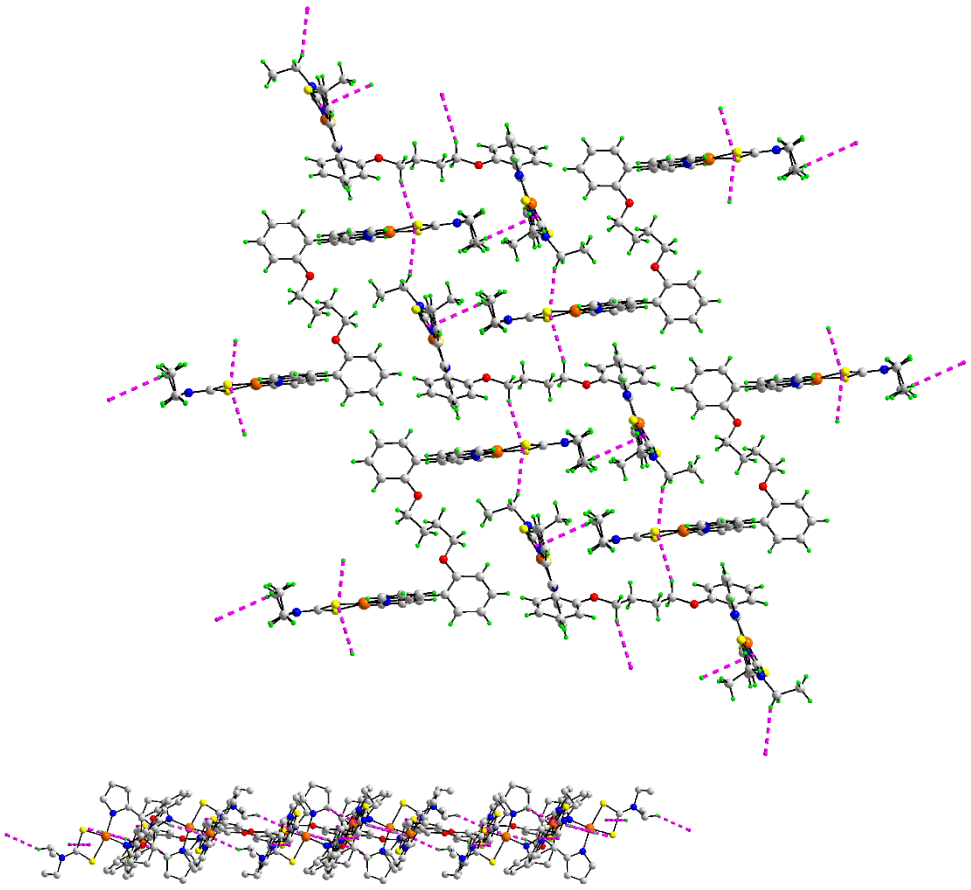




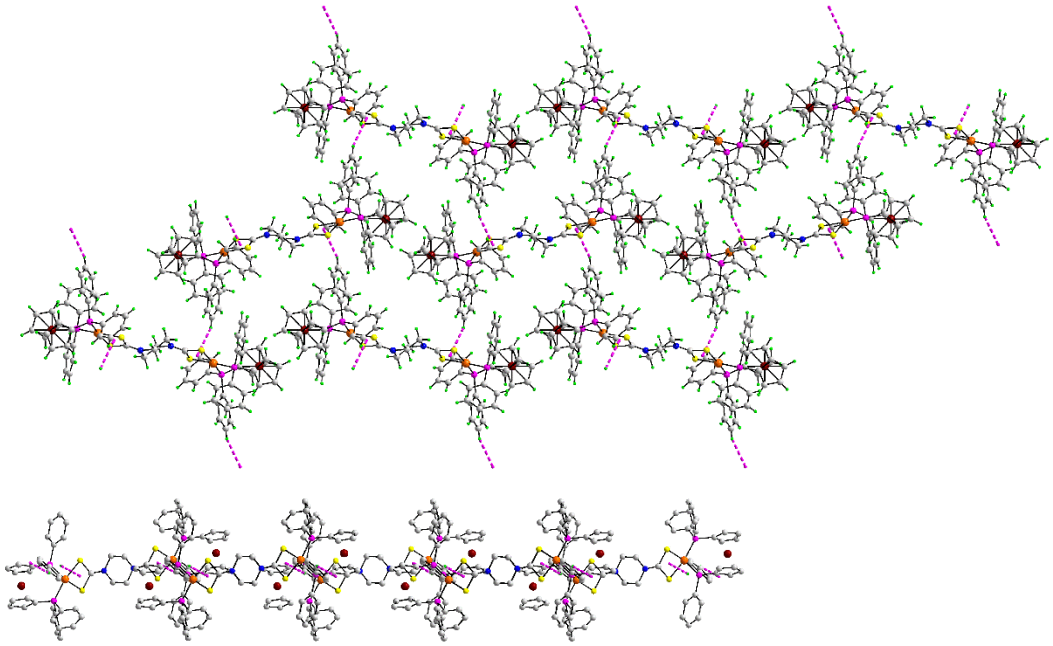
123. BEMHOS: (Allyl(cyclohexyl)carbamodithioato)-(isothiocyanato)-(triphenylphosphino)-nickel(II)
S. Srinivasan, K. Ramalingam and C. Rizzoli, *Z. Anorg. Allg. Chem.*, 2012, **638**, 1356-1361; doi: 10.1002/zaac.201200103
d = 2.99 Å, C–H···Cg(chelate ring) = 146° and θ = 11°
d = 3.17 Å, C–H···Cg(chelate ring) = 142° and θ = 16°
{The dithiocarbamate ligand accepts both methylene- and N-methylene-C–H···Cg(chelate ring) interactions (first and second entries, respectively) donated by the cyclohexyl and allyl substituents derived from symmetry related dithiocarbamate ligands. At the same time, the substituents bridge different dithiocarbamate ligands, one of which is already connected through a centre of inversion. In summary, each dithiocarbamate ligand is associated *via* C–H···Cg(chelate ring) interactions with three other dithiocarbamate ligands (molecules) with the result double-layer is formed}



124. RULMIU: Benzeneselenato-diethyldithiocarbamato-triphenylphosphino-nickel(II)
S. Babikanyisa and J. Darkwa, *Inorg. Chim. Acta*, 1997, **256**, 15-20; doi: 10.1016/S0020-1693(96)05408-4
d = 2.95 Å, C–H···Cg(chelate ring) = 165° and θ = 13°
d = 3.21 Å, C–H···Cg(chelate ring) = 137° and θ = 15°
{The dithiocarbamate accepts two phosphino-phenyl-C–H···Cg(chelate ring) interactions while the phosphino ligand donates two. As these extend laterally, a 2-D array ensues}



125. WAMTAI: [μ_2-((2H-pyrrol-2-ylidene)(2-(4-(2-((1H-pyrrol-2-yl)(2H-pyrrol-2-ylidene)methyl)-phenoxy)butoxy)phenyl)methyl)-1H-pyrrolato]-bis(diethylcarbamodithioato)-di-nickel(II)
R. P. Paitandi, R. S. Singh, S. Mukhopadhyay, A. Kumar and D. S. Pandey, *Dalton Trans.*, 2017, **46**, 5420-5430; doi: 10.1039/C7DT00107J
d = 2.79 Å, C–H···Cg(chelate ring) = 148° and θ = 14°
d = 3.10 Å, C–H···Cg(chelate ring) = 161° and θ = 16°
d = 3.29 Å, C–H···Cg(chelate ring) = 117° and θ = 14°
{There are two independent bi-nuclear molecules comprising the asymmetric unit, each disposed about a centre of inversion, *i.e.* two independent dithiocarbamate ligands. One dithiocarbamate accepts N-methylene-C–H···Cg(chelate ring) and O-methylene-C–H···Cg(chelate ring) interactions (first and second entries) derived from two different molecules of the second independent species. The dithiocarbamate ligands of second independent molecule each accepts a methyl-C–H···Cg(chelate ring) interaction, derived from two different first independent molecules. These interactions extend laterally to assemble molecules into a 2-D array}

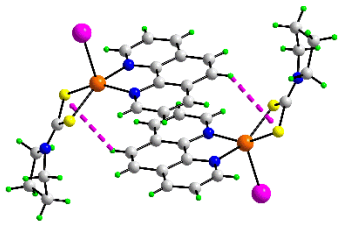


126. RUDLOS: [μ_2-Piperazine-1,4-bis(dithiocarbamato)]-bis[1,1'-bis(diphenylphosphino)ferrocene]-di-nickel(II) bis(hexafluorophosphate) dichloromethane solvate

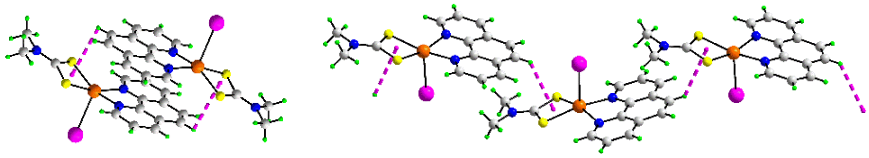
E. R. Knight, N. H. Leung, Y. H. Lin, A. R. Cowley, D. J. Watkin, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, pp. 3688-3697; doi: 10.1039/b821947h

d = 3.08 Å, C–H···Cg(chelate ring) = 137° and θ = 11°

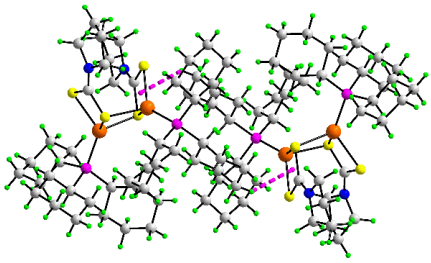
{The nickel atoms are linked by a centrosymmetric, bi-functional dithiocarbamate ligand. Each dithiocarbamate di-anion accepts and donates two phosphino-phenyl-C–H···Cg(chelate ring) interactions, which extend laterally to form a 2-D array}



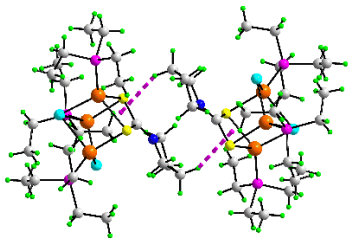
127. XUGWIG: Iodido-(1,10-phenanthroline)-(pyrrolidine-1-carbodithioato)-copper(II)
L.-Q. Fan, J.-H. Wu, J.-M. Lin and Y.-F. Huang, *Chin. J. Struct. Chem.*, 2009, **28**, 580-584.
d = 3.08 Å, C–H···Cg(chelate ring) = 115° and θ = 10°
{Two molecules self-associate about a centre of inversion to form a dimeric aggregate *via* phenanthroline-C–H···Cg(chelate ring) interactions to generate a dimeric aggregate}



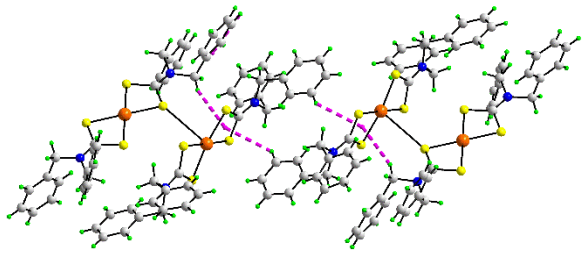
128. TERNOU01: (Dimethyldithiocarbamato)-iodido-(1,10-phenanthroline)copper(II)
L.-Q. Fan and J.-H. Wu, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1768; doi: 10.1107/S1600536807025093
First molecule: *d* = 3.22 Å, C–H···Cg(chelate ring) = 99° and θ = 11°
Second molecule: *d* = 3.05 Å, C–H···Cg(chelate ring) = 128° and θ = 13°
{Two independent molecules comprise the asymmetric unit. The first molecule self-associates about a centre of inversion to form a dimeric aggregate *via* a pair of phenanthroline-C–H···Cg(chelate ring) interactions. Within this dimeric aggregate, there are close five-/six-membered π···π interactions of 3.803(3) Å. The other self-associates into a helical (2_1) chain *via* phenanthroline-C–H···Cg(chelate ring) interactions}



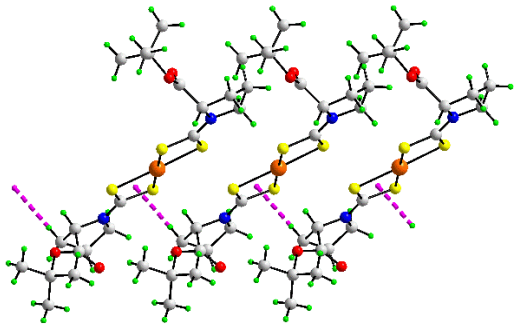
129. MEWNEK: bis(μ$_2$-Pyrrolidine-1-carbodithioato)-bis(tricyclohexylphosphane)-di-copper(I)
Y. J. Tan, C. I. Yeo, N. R. Halcovitch and E. R. T. Tiekink, *Z. Kristallogr. - New Cryst. Struct.*, 2018, **233**, 513-515; doi: 10.1515/ncrs-2017-0406
d = 2.98 Å, C–H···Cg(chelate ring) = 152° and θ = 19°
{Centrosymmetrically related molecules are connected by a pair of methylene-C–H···Cg(chelate ring) interactions to generate a supramolecular dimer}



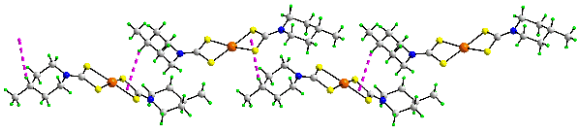
130. WATSOC: (μ-pyrrolidine-1-carbodithioato)-bis(μ-chlorido)-tris(triethylphosphane)-tri-copper(I)
Y. J. Tan, C. I. Yeo, N. R. Halcovitch, M. M. Jotani and E. R. T. Tiekink, *Acta Crystallogr., Sect. E: Cryst. Commun.*, 2017, **73**, 720-725; doi: 10.1107/S2056989017005382
d = 2.83 Å, C–H···Cg(chelate ring) = 148° and θ = 5°
{Two molecules self-associate about a centre of inversion to form a dimeric aggregate *via* methylene-C–H···Cg(chelate ring) interactions to generate a dimeric aggregate}



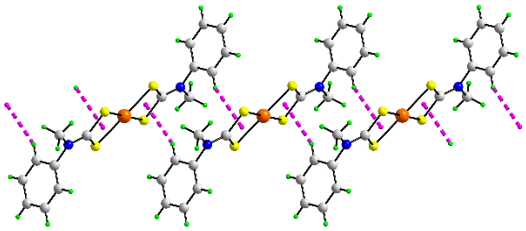
131. UKEDIX: bis(Dibenzyldithiocarbamato)copper(II)
S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano and J. T. Welch, *Polyhedron*, 2003, **22**, 1575-1583; doi: 10.1016/S0277-5387(03)00264-X
d = 3.01 Å, C–H···Cg(chelate ring) = 158° and θ = 16°
d = 3.10 Å, C–H···Cg(chelate ring) = 132° and θ = 10°
{Two formula units are connected by a weak Cu···S interaction of 3.47 Å as well as a N-methylene-C–H···Cg(chelate ring) interaction. Two centrosymmetrically related two-molecule aggregates are connected by a pair of phenyl-C–H···Cg(chelate ring) interactions}



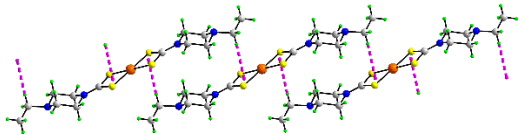
132. LIPWOZ: bis[2-(t-Butoxycarbonyl)pyrrolidine-1-carbodithioato]copper(II)
L. Brustolin, C. Nardon, N. Pettenuzzo, N. Zuin Fantoni, S. Quarta, F. Chiara, A. Gambalunga, A. Trevisan, L. Marchio, P. Pontisso and D. Fregona, *Dalton Trans.*, 2018, **47**, 15477-15486; doi: 10.1039/C8DT02965B
d = 2.70 Å, C–H···Cg(chelate ring) = 179° and θ = 14°
{Each molecule donates one and accepts one methylene-C–H···Cg(chelate ring) interaction on either side of one chelate ring to generate a chain with a linear topology}



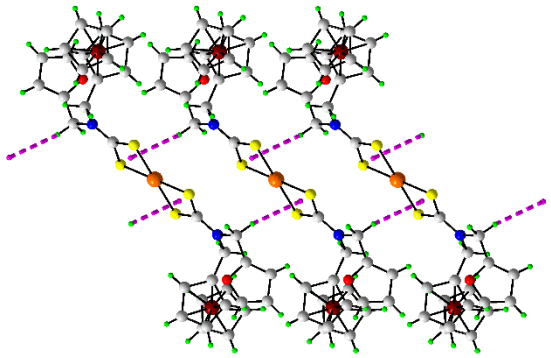
133. EWETAD: bis(4-Methylpiperidine-1-carbodithioato)copper(II)
P. Nath, M. K. Bharty, B. Maiti, A. Bharti, R. J. Butcher, J. L. Wikaira and N. K. Singh, *RSC Advances*, 2016, **6**, 93867-93880; doi: 10.1039/C6RA15186H
d = 3.08 Å, C–H···Cg(chelate ring) = 148° and θ = 19°
{Each centrosymmetric, binuclear molecule, one chelate ring accepts and the second dithiocarbamate ligand donates one methine-C–H···Cg(chelate ring) interaction generate a helical (2_1) supramolecular chain}



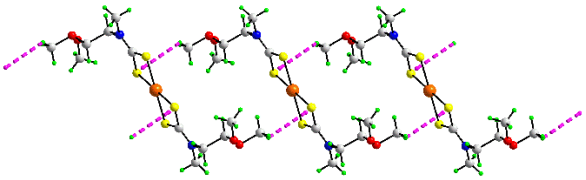
134. MPTCCU: bis[Methyl(phenyl)carbamodithioato]-copper(II)
J. M. Martin, P. W. G. Newman, B. W. Robinson and A. H. White, *J. Chem. Soc., Dalton Trans*., 1972, pp. 2233-2238; doi: 10.1039/dt9720002233
d = 2.76 Å, C–H···Cg(chelate ring) = 157° and θ = 10°
{Each centrosymmetric molecule donates two and accepts two phenyl-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}



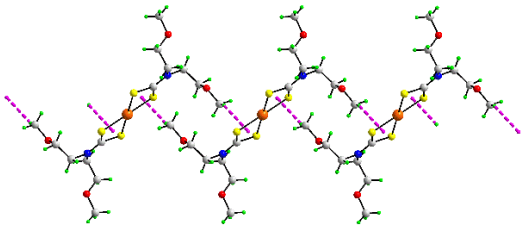
135. JOBBIM: bis(N'-Ethyl-N-piperazinylcarbodithioato)copper(II)
Y. Wang, Y. Lu, C.-Y. Luo, L.-H. Yan and L.-D. Lu, *Chin. J. Inorg. Chem*., 2008, **24**, 691-695.
d = 2.84 Å, C–H···Cg(chelate ring) = 177° and θ = 18°
{Half a centrosymmetric molecule comprises the asymmetric unit. Each dithiocarbamate ligand donates one and accepts one N-methylene-C–H···Cg(chelate ring) interaction to generate a linear chain}



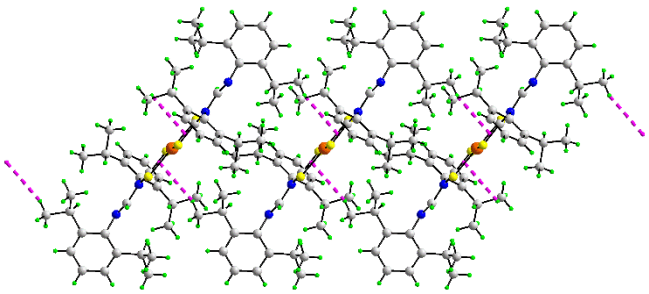
136. GISTAF: bis[((Ferrocen-1-yl)methyl)[(furan-2-yl)methyl]carbamodithioato]copper(II)
V. Singh, R. Chauhan, A. N. Gupta, V. Kumar, M. G. B. Drew, L. Bahadur and N. Singh, *Dalton Trans*., 2014, **43**, 4752-4761; doi: org/10.1039/C3DT52142G
d = 2.88 Å, C–H···Cg(chelate ring) = 163° and θ = 20°
{Each centrosymmetric molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to translationally related molecules to generate a linear chain. See (supramolecular synthon) polymorph, GISTAF01}



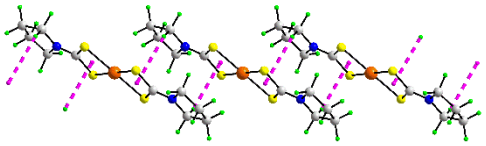
137. IDENIQ: bis[(2,2-Dimethoxyethyl)methylcarbamodithioato]copper(II)
I. P. Ferreira, G. M. de Lima, E. B. Paniago, J. A. Takahashi, K. Krambrock, C. B. Pinheiro, J. L. Wardell and L. C. Visentin, *J. Mol. Struct*., 2013, **1048**, 357-366; doi: 10.1016/j.molstruc.2013.06.006
d = 3.05 Å, C–H···Cg(chelate ring) = 128° and θ = 11°
{The centrosymmetric molecule donates two and accepts two methyoxy-C–H···Cg(chelate ring) interactions on either side of the molecule to generate a linear chain}



138. SOTNEV: bis[bis(2-Methoxyethyl)carbamodithioato]copper(II)
G. Hogarth, E.-J. C.-R. C. R.Rainford-Brent and I. Richards, *Inorg. Chim. Acta*, 2009, **362**, 1361-1364; doi: 10.1016/j.ica.2008.05.010
d = 3.10 Å, C–H···Cg(chelate ring) = 144° and θ = 15°
{Each centrosymmetric molecule donates two and accepts two methoxy-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}

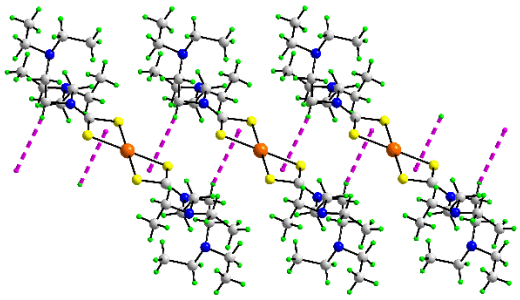


139. LONKUX: bis([2,6-diisopropylphenyl]({[2,6-diisopropylphenyl]imino}methyl)-carbamodithioato)-copper(II)
S. D. Oladipo, B. Omondi and C. Mocktar, *Polyhedron*, 2019, **170**, 712-722; doi: org/10.1016/j.poly.2019.06.038
d = 3.12 Å, C–H···Cg(chelate ring) = 148° and θ = 10°
{Half a centrosymmetric molecule comprises the asymmetric unit. Each dithiocarbamate ligand donates one and accepts one methyl-C–H···Cg(chelate ring) interaction to generate a linear chain}

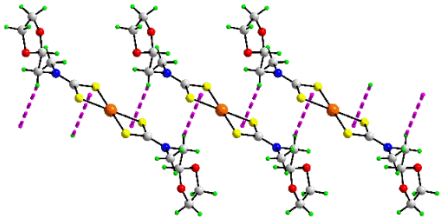


140. PYRCTC: bis(Pyrrolidinecarbodithioato)copper(II)
P. W. G. Newman, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans*., 1973, 1332-1335; doi: 10.1039/DT9730001332

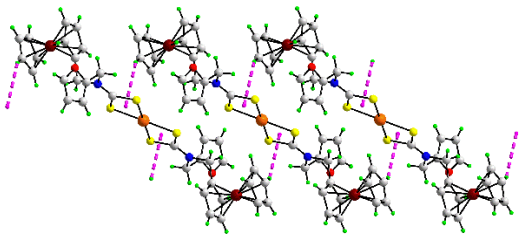
d = 3.13 Å, C–H···Cg(chelate ring) = 125° and θ = 20°
{Each centrosymmetric molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}



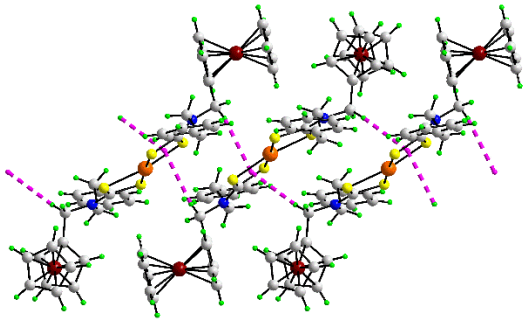
141. QOWXIK: bis[bis(2-(Diethylamino)ethyl)carbamodithioato]copper(II)
G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent, S. E. Kabir, I. Richards, J. D. E. T. Wilton-Ely and Qi Zhang, *Inorg. Chim. Acta*, 2009, **362**, 2020-2026; doi: 10.1016/j.ica.2008.09.030
d = 3.17 Å, C–H···Cg(chelate ring) = 134° and θ = 17°
{Each centrosymmetric molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}



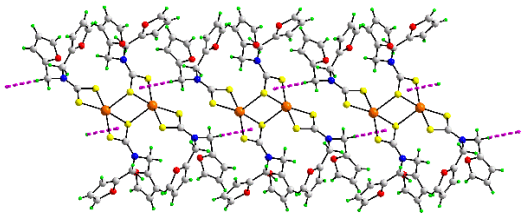
142. IDENOW: bis[(1,3-Dioxolan-2-ylmethyl)methylcarbamodithioato]copper(II)
I. P. Ferreira, G. M. de Lima, E. B. Paniago, J. A. Takahashi, K. Krambrock, C. B. Pinheiro, J. L. Wardell and L. C. Visentin, *J. Mol. Struct*., 2013, **1048**, 357-366; doi: 10.1016/j.molstruc.2013.06.006
d = 3.22 Å, C–H···Cg(chelate ring) = 111° and θ = 15°
{The centrosymmetric molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions on either side of the molecule to generate a linear chain}



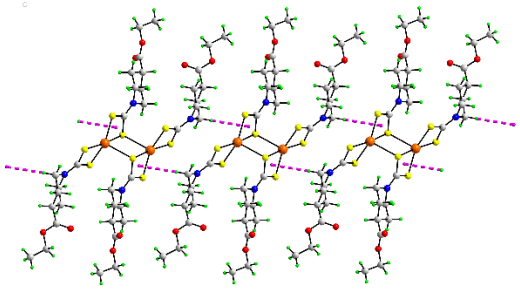
143. GISTAF01: bis[((Ferrocen-1-yl)methyl)[(furan-2-yl)methyl]carbamodithioato]copper(II)
S. K. Verma and V. K. Singh, *J. Organomet. Chem*., 2015, **791**, 214-224; doi: 10.1016/j.jorganchem.2015.05.028
d = 3.23 Å, C–H···Cg(chelate ring) = 138° and θ = 12°
{Each centrosymmetric molecule donates two and accepts two cyclopentadienyl-C–H···Cg(chelate ring) interactions to translationally related molecules to generate a linear chain. See (supramolecular synthon) polymorph, GISTAF}



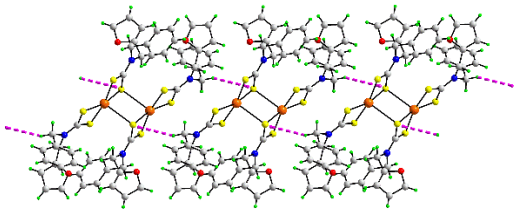
144. QEWJOU: bis[(Ferrocenylmethyl)(2-phenylethyl)carbamodithioato]copper(II)
G. Gurumoorthy, S. Thirumaran and S. Ciattini, *Appl. Organomet. Chem*., 2018, **32**, e4363; doi: 10.1002/aoc.4363
d = 2.80 Å, C–H···Cg(chelate ring) = 153° and θ = 16°
d = 3.02 Å, C–H···Cg(chelate ring) = 138° and θ = 14°
{Two square-planar molecules associate about a centre of inversion to form a supramolecular dimer *via* two N-methylene-C–H···Cg(chelate ring) interactions and these are connected into a twisted supramolecular chain by second pair of N-methylene-C–H···Cg(chelate ring) interactions operating about another centre of inversion, resulting in a twisted chain}



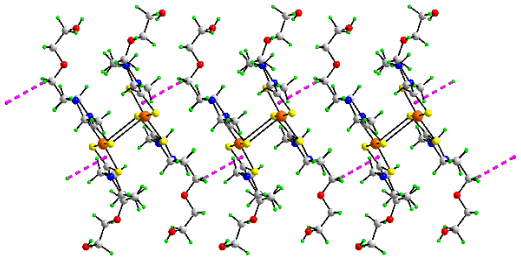
145. MISMAE: bis[μ2-bis(2-Furylmethyl)carbamodithioato]-bis[bis(2-furylmethyl)carbamodithioato]-di-copper(II)
A. N. Gupta, V. Singh, V. Kumar, A. Rajput, L. Singh, M. G. B. Drew and N. Singh, *Inorg. Chim. Acta*, 2013, **408**, 145-151; doi: 10.1016/j.ica.2013.09.006
d = 2.84 Å, C–H···Cg(chelate ring) = 179° and θ = 16°
{Each centrosymmetric, binuclear molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}



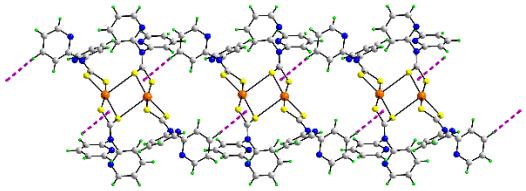
146. MISMUY: bis[μ2-4-(Ethoxycarbonyl)piperidine-1-carbodithioato]-bis[4-(ethoxycarbonyl)piperidine-1-carbodithioato]-di-copper(II)
A. N. Gupta, V. Singh, V. Kumar, A. Rajput, L. Singh, M. G. B. Drew and N. Singh, *Inorg. Chim. Acta*, 2013, **408**, 145-151; doi: 10.1016/j.ica.2013.09.006
d = 3.07 Å, C–H···Cg(chelate ring) = 173° and θ = 19°
{Each centrosymmetric, binuclear molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}



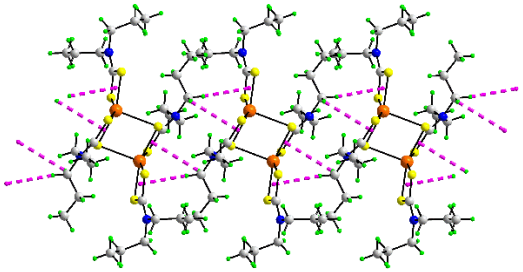
147. MISNAF: bis[μ2-Benzyl(2-furylmethyl)carbamodithioato]-bis[benzyl(2-furylmethyl)carbamodithioato]-di-copper(II)
A. N. Gupta, V. Singh, V. Kumar, A. Rajput, L. Singh, M. G. B. Drew and N. Singh, *Inorg. Chim. Acta*, 2013, **408**, 145-151; doi: 10.1016/j.ica.2013.09.006
d = 3.15 Å, C–H···Cg(chelate ring) = 157° and θ = 17°
{Each centrosymmetric molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}



148. GACPOQ: bis[4-(2-(2-Hydroxyethoxy)ethyl)piperazinedithiocarbamato]copper(II)
A. Mederos, A. Cachapa, R. Hernández-Molina, M. T. Armas, P. Gili, M. Sokolov, J. González-Platas and F. Brito, *Inorg. Chem. Commun.*, 2003, **6**, 498-502; doi: 10.1016/S1387-7003(03)00011-X
d = 3.21 Å, C–H···Cg(chelate ring) = 139° and θ = 7°
{Each centrosymmetric, binuclear molecule donates two and accepts two O-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}

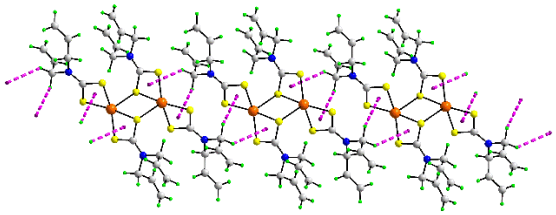


149. ZUWLUY: bis[(2,2'-Dipyridyl)dithiocarbamato]copper(II)
A. M. M. Lanfredi, F. Ugozzoli and A. Camus, *J. Chem. Cryst.*, 1996, **26**, 141-145; doi: 10.1007/BF01669731
d = 3.21 Å, C–H···Cg(chelate ring) = 141° and θ = 17°
{Each centrosymmetric molecule donates two and accepts two pyridyl-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain}

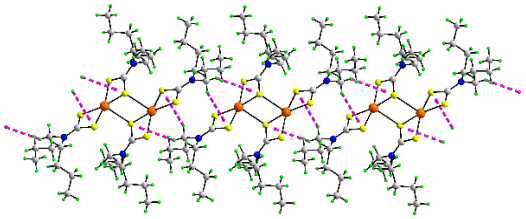


150. PRSCCU11: bis(μ2-Di-n-propyldithiocarbamato)-bis(di-n-propyldithiocarbamato)-di-copper(II)

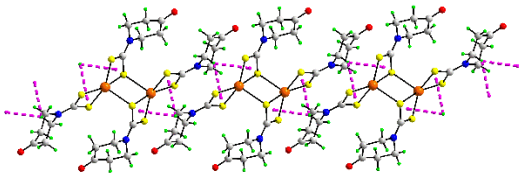
G. Hogarth and S. Faulkner, *Inorg. Chem. Commun*., 2013, **35**, 65-68; doi: 10.1016/j.inoche.2013.05.025
d = 2.82 Å, C–H···Cg(chelate ring) = 165° and θ = 14°
d = 3.26 Å, C–H···Cg(chelate ring) = 100° and θ = 9°
{Each centrosymmetric, binuclear molecule donates four and accepts four N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain. In essence, methylene groups straddle two chelate rings employing both hydrogen atoms}



151. CUPFAU: bis(μ$_2$-Diallyldithiocarbamato)-bis(diallyldithiocarbamato)-di-copper(II)
E. Kellö, V. Kettmann and J. Garaj, *Collect. Czech. Chem. Commun*., 1984, **49**, 2210-2221; doi: 10.1135/cccc19842210
d = 3.01 Å, C–H···Cg(chelate ring) = 134° and θ = 12°
d = 3.23 Å, C–H···Cg(chelate ring) = 116° and θ = 11°
{Each centrosymmetric, binuclear molecule donates four and accepts four N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain. In essence, employing two methylene-hydrogen atoms, as the methylene groups straddle two chelate rings. Hydrogen atom positions were generated in *Mercury*}

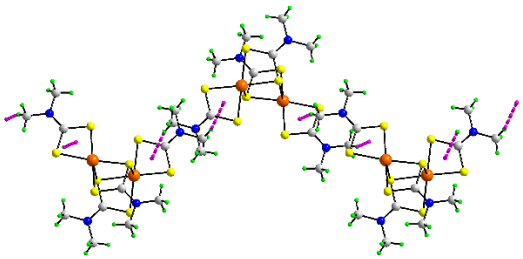


152. UKECUI: bis(μ$_2$-Di-*n*-butyldithiocarbamato)-bis(di-*n*-butyldithiocarbamato)-di-copper(II)
S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano and J. T. Welch, *Polyhedron*, 2003, **22**, 1575-1583; doi: 10.1016/S0277-5387(03)00264-X
d = 3.02 Å, C–H···Cg(chelate ring) = 147° and θ = 18°
d = 3.08 Å, C–H···Cg(chelate ring) = 121° and θ = 7°
{Each centrosymmetric molecule donates four and accepts four N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain. Each participating methylene employs both hydrogen atoms to straddle two chelate rings}

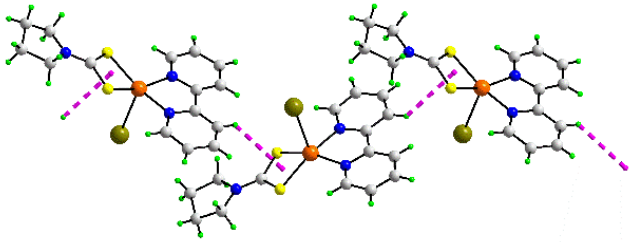


153. MESSAF: bis[μ$_2$-(3-Oxopentan-1,5-diyl)dithiocarbamate]-bis[μ$_2$-N,N-(3-oxopentan-1,5-diyl)dithiocarbamate]-di-copper(II)
A. Cachapa, A. Mederos, P. Gili, R. Hernández-Molina, S. Domínguez, E. Chinea, M. López Rodríguez, M. Feliz, R. Llusar, F. Brito, C. M. R. de Galarreta, C. Tarbraue and G. Gallardo, *Polyhedron*, 2006, **25**, 3366-3378; doi: 10.1016/j.poly.2006.06.008
d = 2.81 Å, C–H···Cg(chelate ring) = 154° and θ = 18°

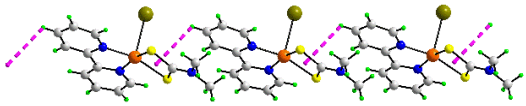
d = 2.90 Å, C–H···Cg(chelate ring) = 140° and θ = 19°
{Each centrosymmetric, binuclear molecule donates four and accepts four N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a linear chain. In this case, the participating methylene-C–H atoms are bifurcated}



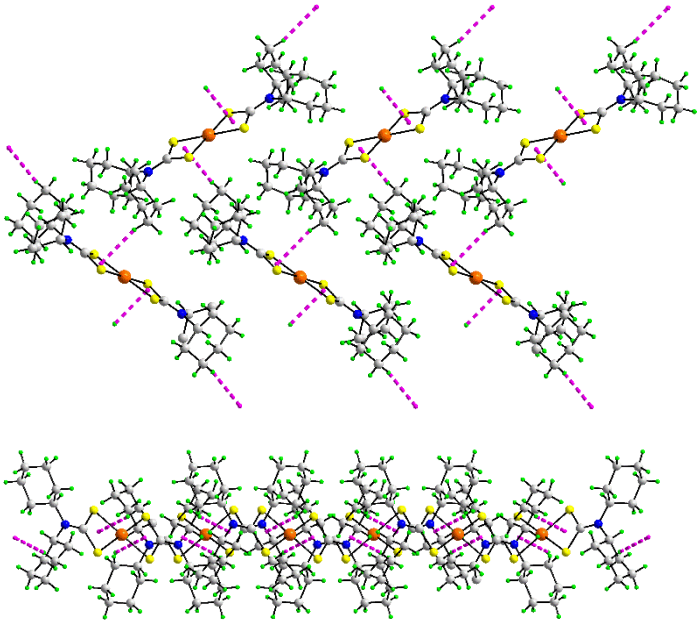
154. GOGQAV: bis(μ2-Dimethyldithiocarbamato)-bis(dimethyldithiocarbamato)copper(II)
L.-Q. Fan and J.-H. Wu, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2009, **65**, m319; doi: 10.1107/S1600536809006230
d = 3.10 Å, C–H···Cg(chelate ring) = 158° and θ = 19°
{Each binuclear molecule, generated by 2-fold symmetry, donates two and accepts two methyl-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a chain with a zig-zag topology (glide symmetry)}



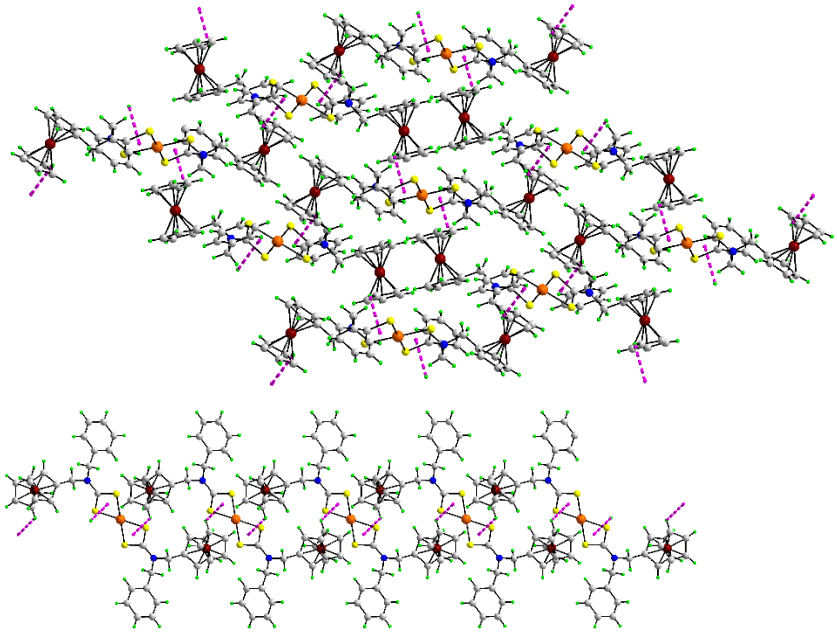
155. BIZCOD: (2,2'-Bipyridine)-iodido-(pyrrolidine-1-dithiocarboxylato)copper(II)
L.-Q. Fan and J.-H. Wu, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, **64**, m639; doi: 10.1107/S1600536808008945
d = 3.11 Å, C–H···Cg(chelate ring) = 133° and θ = 20°
{Each molecule donates one and accepts one pyridyl-C–H···Cg(chelate ring) interaction on either side of the molecule to generate a chain with a helical (2_1) topology}



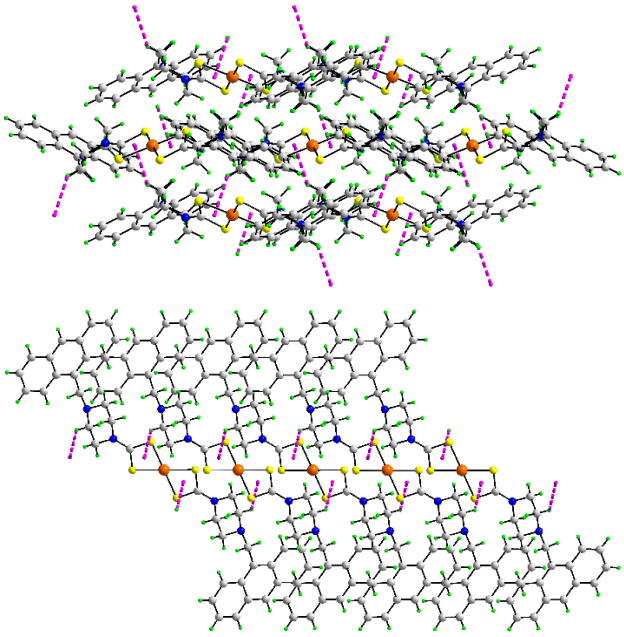
156. CABPAY: (2,2'-Bipyridine)-(dimethyldithiocarbamato)-iodido-copper(II)
L.-Q. Fan and J.-H. Wu, *Z. Kristallogr.-New Cryst. Struct.*, 2010, **225**, 347-348; doi: 10.1524/ncrs.2010.0151
d = 3.21 Å, C–H···Cg(chelate ring) = 116° and θ = 11°
{Each molecule donates one and accepts one pyridyl-C–H···Cg(chelate ring) interaction on either side of the molecule to generate a chain with a linear topology}



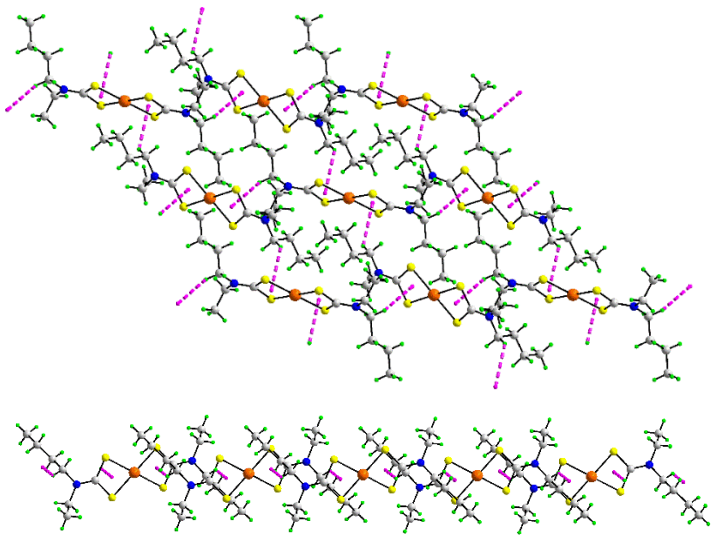
157. UKEDET: bis(Dicyclohexyldithiocarbamato)copper(II)
S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano and J. T. Welch, *Polyhedron*, 2003, **22**, 1575-1583; doi: 10.1016/S0277-5387(03)00264-X
d = 2.69 Å, C–H···Cg(chelate ring) = 162° and θ = 12°
{Each centrosymmetric molecule donates two and accepts two methylene-C–H···Cg(chelate ring) interactions extending laterally to generate a 2-D array}



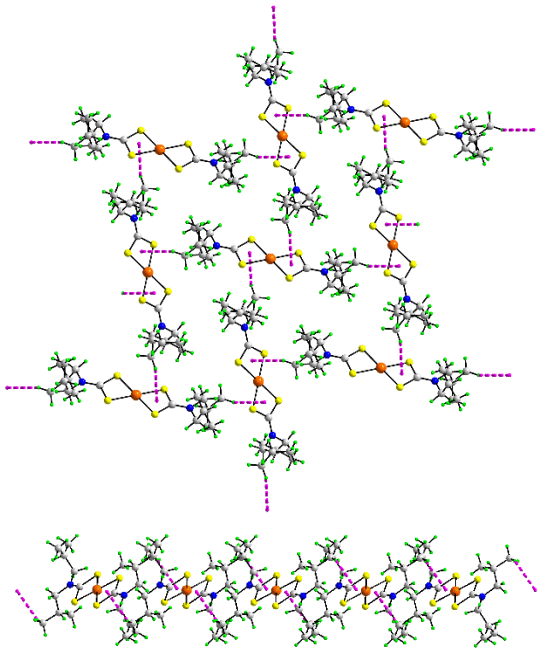
158. MUYXIO: bis(N-Benzyl-N-ferrocenyldithiocarbamato)copper(II)
A. Kumar, R. Chauhan, K. C. Molloy, G. Kociok-Kohn, L. Bahadur, N. Singh, *Chem.-Eur. J.*, 2010, **16**, 4307-4314; doi: 10.1002/chem.200903367
d = 2.92 Å, C–H···Cg(chelate ring) = 107° and θ = 2°
{Each centrosymmetric molecule donates two and accepts two cyclopentadienyl-C–H···Cg(chelate ring) interactions extending laterally to form a two-dimensional array}



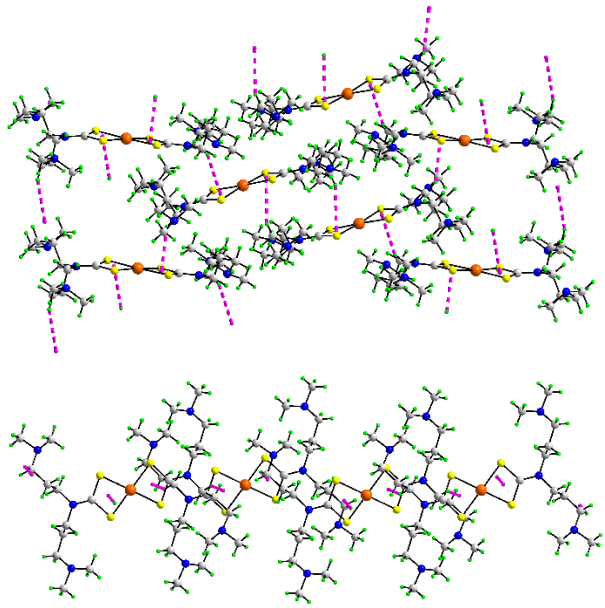
159. SEQQIP: bis[4-(Anthracen-9-ylmethyl)piperazine-1-dithiocarbamato]copper(II)
M. H. Lim and S. J. Lippard, *Inorg. Chem*., 2006, **45**, 8980-8989; doi: 10.1021/ic0609913
d = 3.11 Å, C–H···Cg(chelate ring) = 128° and θ = 10°
{Each centrosymmetric, square planar molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions to either side of the molecule to generate a 2-D array with a flat topology}



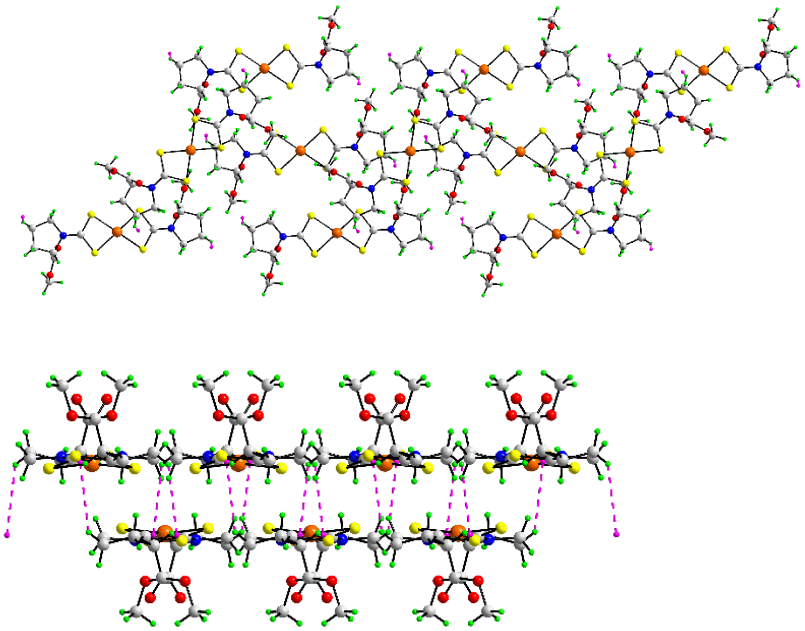
160. UKEDOD: bis(N-Butyl-N-ethyldithiocarbamato)copper(II)
S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano and J. T. Welch, *Polyhedron*, 2003, **22**, 1575-1583; doi: 10.1016/S0277-5387(03)00264-X
d = 3.13 Å, C–H···Cg(chelate ring) = 130° and θ = 6°
{Each centrosymmetric molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions extending laterally to generate a 2-D array}



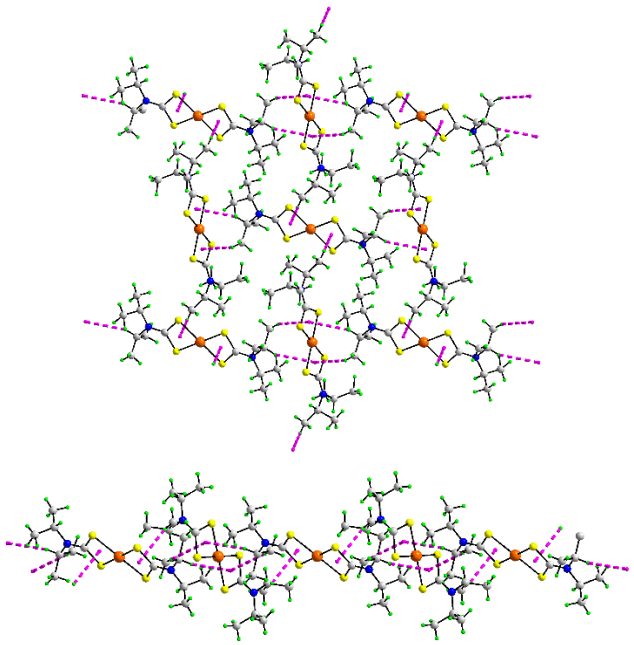
161. UKEDAP: bis[Diisobutyldicarbamodithioato]copper(II)
S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano and J. T. Welch, *Polyhedron*, 2003, **22**, 1575-1583; doi: 10.1016/S0277-5387(03)00264-X
d = 3.18 Å, C–H···Cg(chelate ring) = 145° and θ = 9°
{Each centrosymmetric molecule donates two and accepts two methyl-C–H···Cg(chelate ring) interactions extending laterally to generate a 2-D array}



162. QOWXOQ: bis(bis(3-(Dimethylamino)propyl)carbamodithioato)copper(II)
G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent, S. E. Kabir, I. Richards, J. D. E. T. Wilton-Ely and Qi Zhang, *Inorg. Chim. Acta*, 2009, **362**, 2020-2026; doi: 10.1016/j.ica.2008.09.030
d = 2.91 Å, C–H···Cg(chelate ring) = 143° and θ = 8°
d = 3.00 Å, C–H···Cg(chelate ring) = 142° and θ = 19°
{Square-planar molecules associate *via* N-methylene-C–H···Cg(chelate ring) interactions involving both chelate rings to form a supramolecular layer with a flat topology}

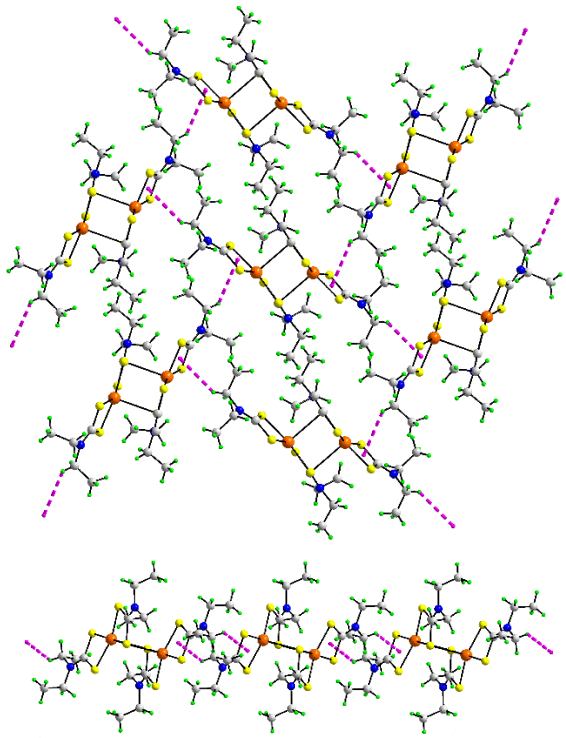


163. LIPTEM: bis[2-(Methoxycarbonyl)pyrrolidine-1-carbodithioato]copper(II)
L. Brustolin, C. Nardon, N. Pettenuzzo, N. Zuin Fantoni, S. Quarta, F. Chiara, A. Gambalunga, A. Trevisan, L. Marchio, P. Pontisso and D. Fregona, *Dalton Trans*., 2018, **47**, 15477-15486; doi: 10.1039/C8DT02965B
d = 3.20 Å, C–H···Cg(chelate ring) = 128° and θ = 9°
{The Cu atom lies on a 2-fold axis; each molecule donates two and accepts two methylene-C–H···Cg(chelate ring) interactions orientated to the same side of the molecule to connect laterally related molecules to generate a double-layer with a flat topology}

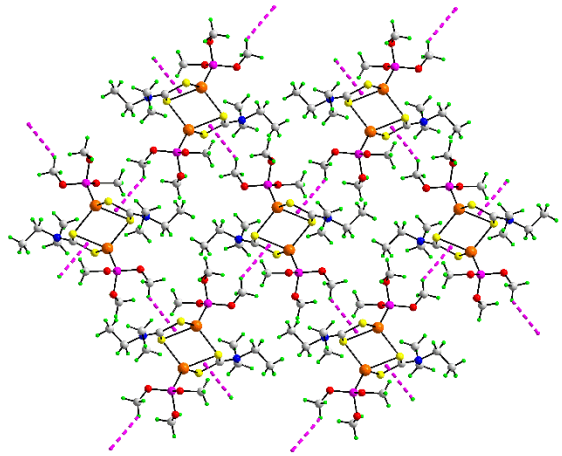


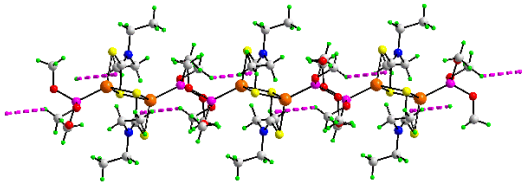
164. NDTCCU: bis(Diisopropyldithiocarbamato)copper(II)
H. Iwasaki and K. Kobayashi, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem*., 1980, **36**, 1655-1657; doi: 10.1107/S0567740880006826
d = 2.91 Å, C–H···Cg(chelate ring) = 154° and θ = 15°
d = 3.15 Å, C–H···Cg(chelate ring) = 158° and θ = 14°

d = 3.17 Å, C–H···Cg(chelate ring) = 155° and θ = 17°
{Two, independent centrosymmetric molecules comprise the asymmetric unit. One molecule accepts two methyl-C–H···Cg(chelate ring) interactions while donating two methine-C–H···Cg(chelate ring) and two methyl-C–H···Cg(chelate ring) interactions to two different molecules of the second independent molecule whereby, the methine and methyl-hydrogen atoms of one residue spans both chelate rings. This results in the formation of two-dimensional array with a flat topology}



165. CETCAM01: bis(μ2-Diethyldithiocarbamato)-bis(diethyldithiocarbamato)-di-copper(II)
F. Jian, Z. Wang, Z. Bai, X. You, H.-K. Fun, K. Chinnakali and I. A. Razak, *Polyhedron*, 1999, **18**, 3401-3406; doi: 10.1016/S0277-5387(99)00242-9
d = 3.13 Å, C–H···Cg(chelate ring) = 122° and θ = 19°
{Each centrosymmetric, binuclear molecule donates two and accepts two N-methylene-C–H···Cg(chelate ring) interactions extending laterally to generate a planar two-dimensional array}





166. ICOMIY: bis(μ2-Diethyldithiocarbamato)-bis(trimethylphosphito)-di-copper(I)
M. Afzaal, C. L. Rosenberg, M. A. Malik, A. J. P. White and P. O'Brien, *New J. Chem*., 2011, **35**, 2773-2780; doi: 10.1039/c1nj20586b
d = 2.95 Å, C–H···Cg(chelate ring) = 123° and θ = 18°
{Each centrosymmetric, binuclear molecule donates two and accepts two methoxy-C–H···Cg(chelate ring) interactions which extend laterally to generate a two-dimensional array with slightly corrugated topology}