

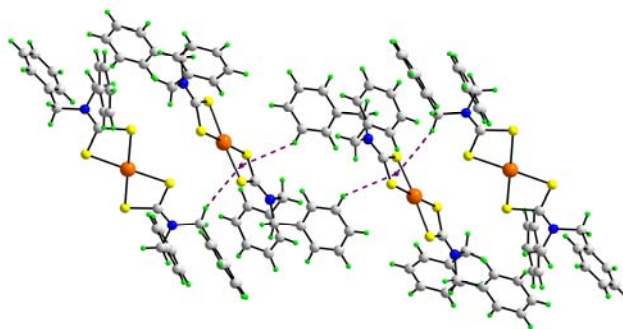
**Emerging supramolecular synthons: C–H... π (chelate) interactions as
supramolecular synthons in metal bis(1,1-dithiolates)†**

Edward R.T. Tiekink^{a*} and Julio Zukerman-Schpector

Electronic Supplementary Material

**SUPRAMOLECULAR AGGREGATION BASED ON C-H... π (chelate)
INTERACTIONS IN PLANAR BIS DITHIOCARBAMATES**

MOTIF (I) – Isolated tetra molecular aggregate



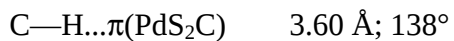
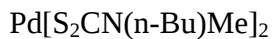
$\text{Pd}[\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2]_2$

$\text{C}-\text{H}\cdots\pi(\text{PdS}_2\text{C})$ 3.04 Å; 132° & 3.06 Å; 159°

F. Shaheen, A. Badshah, M. Gielen, M. Dusek, K. Fejfarova, D. de Vos, and B. Mirza, *J. Organomet. Chem.*, 2007, **692**, 3019; CSD REFCODE: LIGSEA.

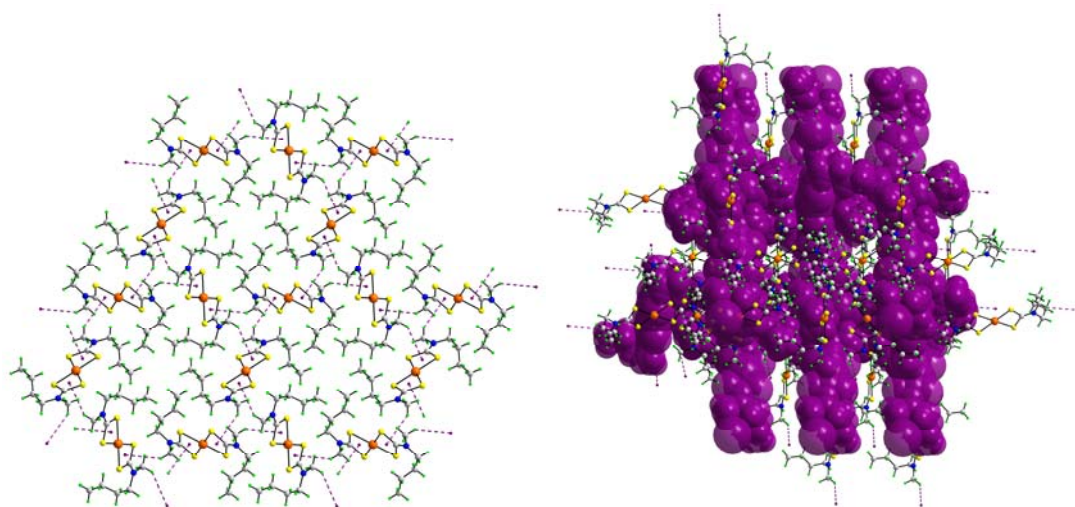
MOTIF (II) – 3D architecture

TRANSITION METAL COMPLEX



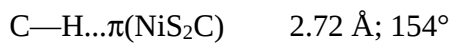
A. Birri, B. Harvey, G. Hogarth, E. Subasi, and F. Ugur, *J. Organomet. Chem.*, 2007,

692, 2448; CSD REFCODE: ODOYAI.



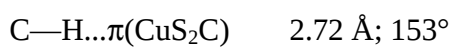
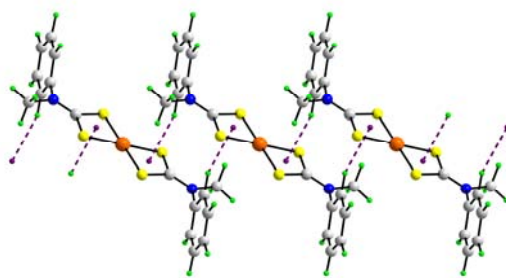
MOTIF (III) – Supramolecular chain

TRANSITION METAL COMPLEXES

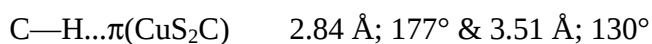
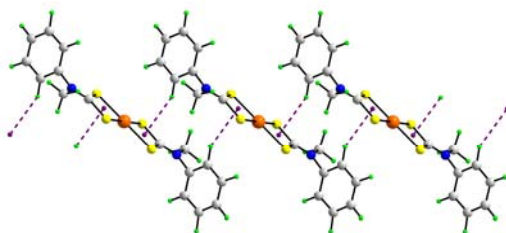


J. M. Martin, P. W. G. Newman, B. W. Robinson, and A. H. White, *J. Chem. Soc.,*

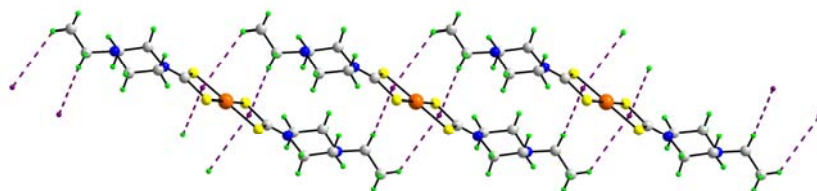
Dalton Trans., 1972, 2233; CSD REFCODE: MPTCNI. Isomorphous with MPTCCU.



J. M. Martin, P. W. G. Newman, B. W. Robinson, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 2233; CSD REFCODE: MPTCCU. Isomorphous with MPTCNI.



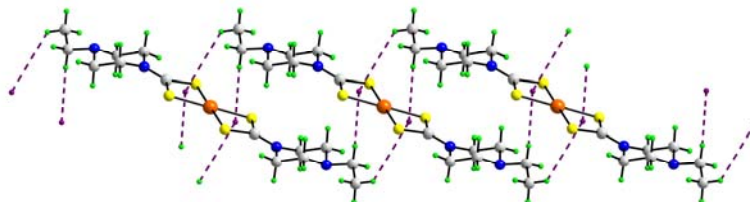
Y. Wang, Y. Lu, C.-Y. Luo, L.-H. Yan, and L.-D. Lu, *Wuji Huaxue Xuebao* (Chin. J. Inorg. Chem.), 2008, **24**, 691; CSD REFCODE: JOBBIM. Isomorphous with MEPGUK.



C—H... π (NiS₂C) 2.86 Å; 176° & 3.52 Å; 130°

Y. Wang and L.-H. Yan, *Jiegou Huaxue (Chin. J. Struct. Chem.)*, 2006, **5** 1260; CSD

REFCODE: MEPGUK. Isomorphous with JOBBIM.

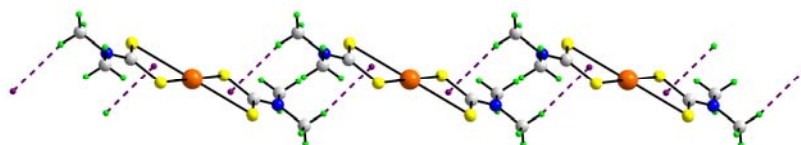


Hg[S₂CNMe₂]₂

C—H... π (HgS₂C) 2.94 Å; 159°

M. J. Cox and E. R. T. Tiekink, *Z. Kristallogr.*, 1997, **212**, 542; CSD REFCODE:

ROQNEQ.

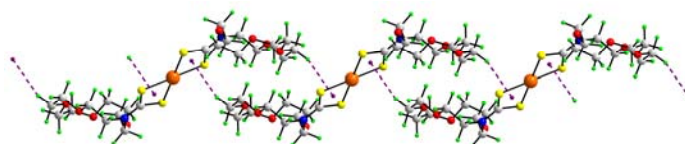


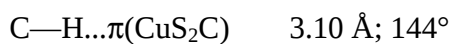
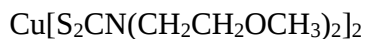
Pt[S₂CN(CH₂CH₂OCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₂CH₂)]₂.2CH₂Cl₂

C—H... π (PtS₂C) 3.05 Å; 158°

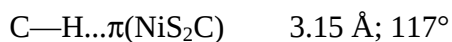
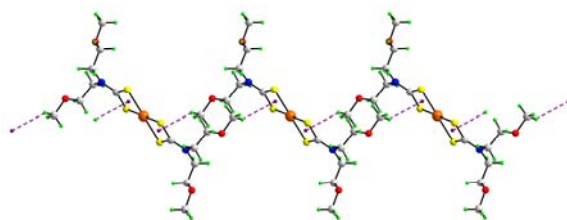
U. Castellato and R. Graziani, *Z. Kristallogr. - New Cryst. Struct.*, 1999, **214**, 495; CSD

REFCODE: QUIXIC. The dichloromethane molecules of solvation are omitted.

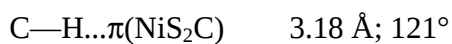
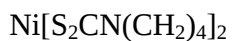
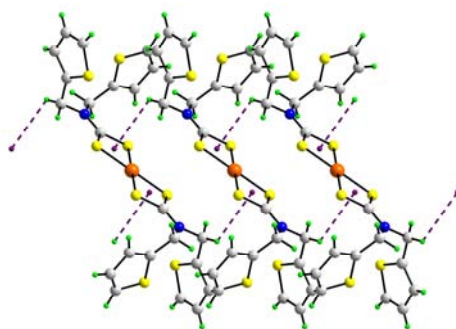




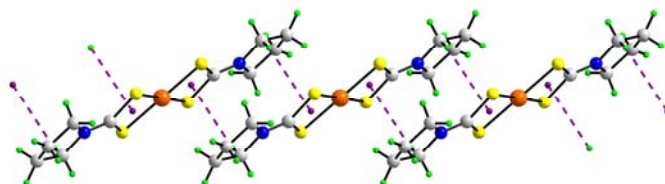
G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent, and I. Richards, *Inorg. Chim. Acta*, 2009, **362**, 1361; CSD REFCODE: SOTNEV.



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. Get. Soedin., SSSR (Chem. Heterocycl. Compd.)*, 1987, 902; CSD REFCODE: GIGWIC.



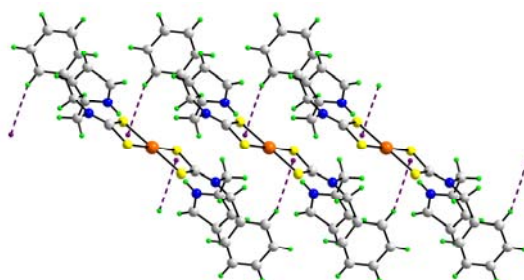
L. M. Engelhardt, J. M. Patrick, and A. H. White, *Aust. J. Chem.*, 1985, **38**, 1413 & P. W. G. Newman, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 1332;
CSD REFCODES: PYRCTN01/PYRCTN. Isomorphous with PYRCTC/PYRCTC01.



$\text{Ni}\{\text{S}_2\text{CN}(\text{CH}_2\text{Ph})\text{CH}_2[\text{c-CN}(\text{H})\text{C}(\text{H})=\text{C}(\text{H})\text{C}(\text{H})=]_4\}_2$

$\text{C—H}\cdots\pi(\text{NiS}_2\text{C})$ 3.19 Å; 150°

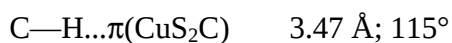
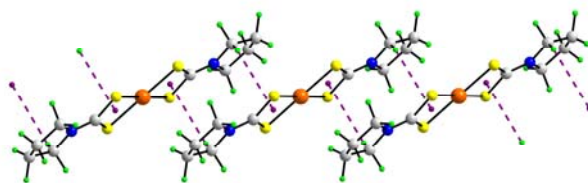
P. D. Beer, A. G. Cheetham, M. G. B. Drew, O. D. Fox, E. J. Hayes, and T. D. Rolls,
Dalton Trans., 2003, 603; CSD REFCODE: QAHFOV.



$\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$

$\text{C—H}\cdots\pi(\text{CuS}_2\text{C})$ 3.30 Å; 118°

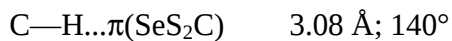
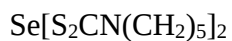
L. M. Engelhardt, J. M. Patrick, and A. H. White, *Aust. J. Chem.*, 1985, **38**, 1413 & P. W. G. Newman, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 1332;
CSD REFCODES: PYRCTC01/PYRCTC. Isomorphous with PYRCTN/PYRCTN01.



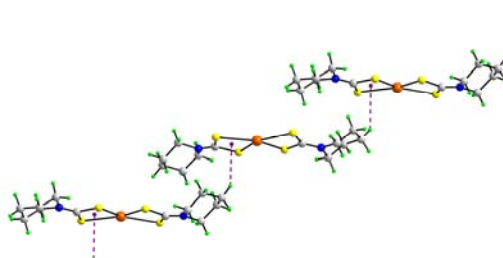
F. W. B. Einstein and J. S. Field, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1974, **30**, 2928; CSD REFCODE: DMTCCU.



MAIN GROUP ELEMENT COMPOUND

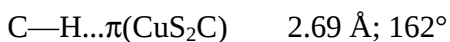


S. P. Chidambaram, G. Aravamudan, and M. Seshasayee, *Z. Kristallogr.*, 1989, **187**, 231;
CSD REFCODE: SEBCAD. Isostructural with YISPEW.

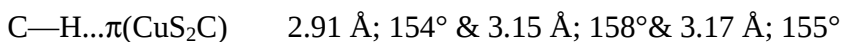
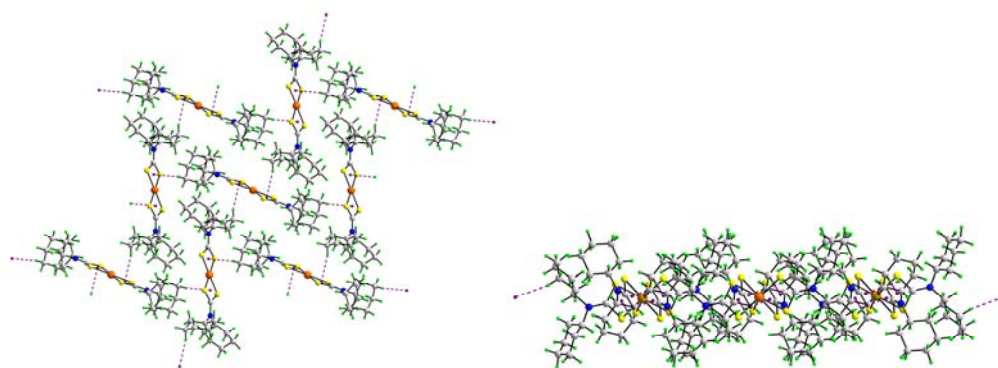


MOTIF (IV) – Supramolecular array

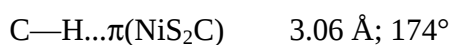
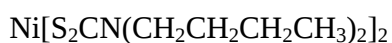
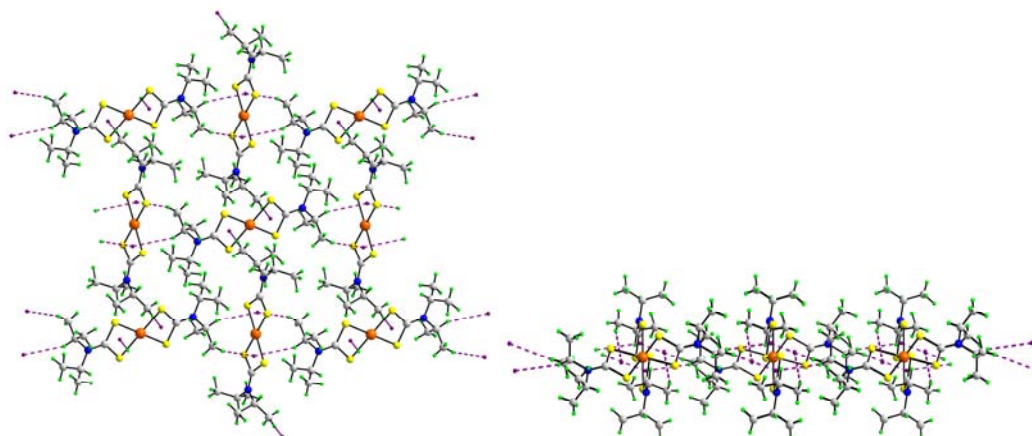
TRANSITION METAL COMPLEXES



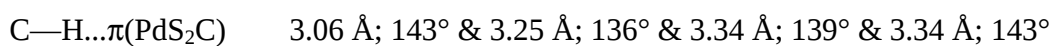
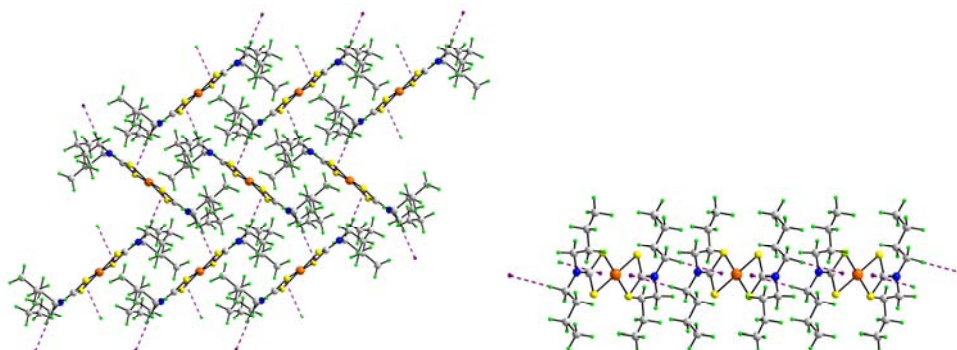
S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano, and J. T. Welch, *Polyhedron*, 2003, **22**, 1575; CSD REFCODE: UKEDET.



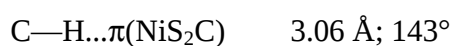
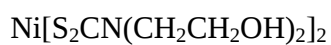
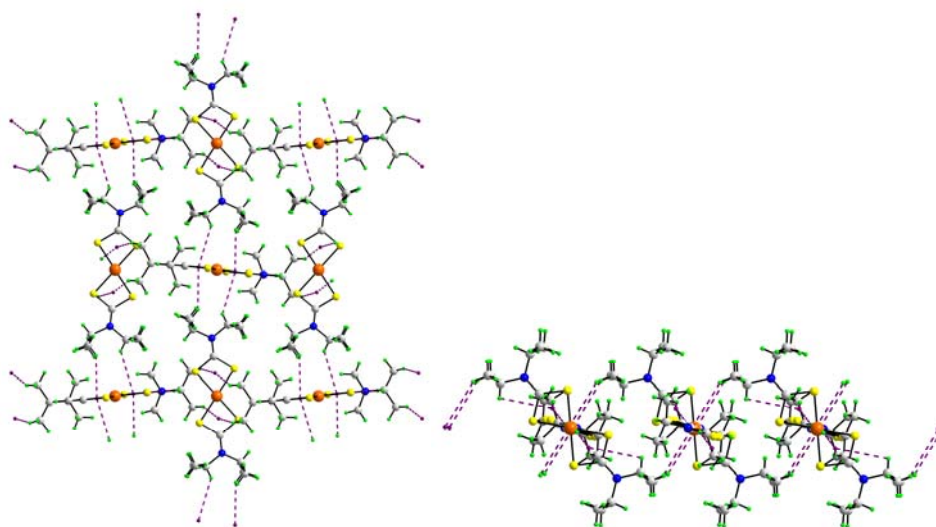
H. Iwasaki and K. Kobayashi, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem*, 1980, **36**, 1655; W. E. Hatfield, P. Singh, and F. Nepveu, *Inorg. Chem.*, 1990, **29**, 4214; F. F. Jian, Z.-X. Wang, Z.-P. Bai, X.Z. You, H.-K. Fun, K. Chinnakali, and I. A. Razak, *Polyhedron*, 1999, **18**, 3401; CSD REFCODES: NDTCCU/NDTCCU01/NDTCCU02.



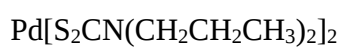
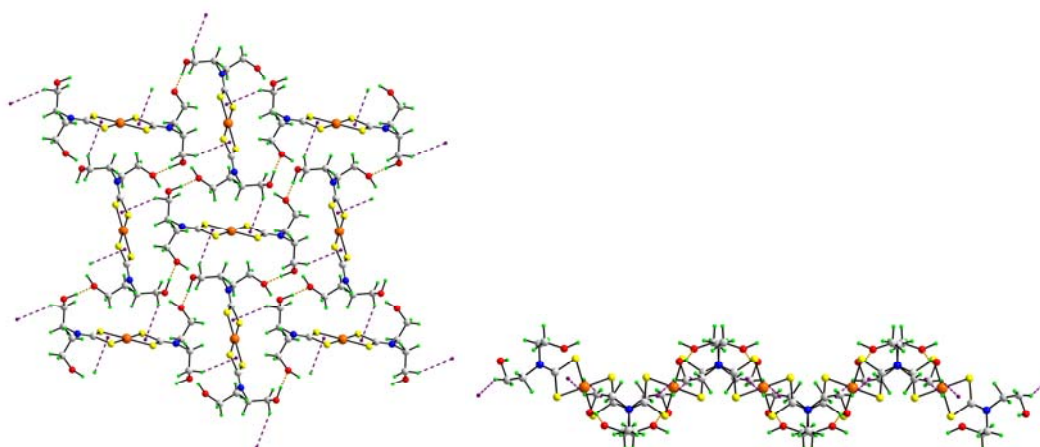
J. Lokaj, V. Vrabel, and E. Kello, *Chem. Zvesti*, 1984, **38**, 313; CSD REFCODE: CIYSEI.



F.-F. Jian, F. Bei, P. Zhao, X. Wang, H.-K. Fun, and K. Chinnakali, *J. Coord. Chem.*, 2002, **55**, 429; CSD REFCODE: UFEWEH01. Isomorphous with IPTCNI10.



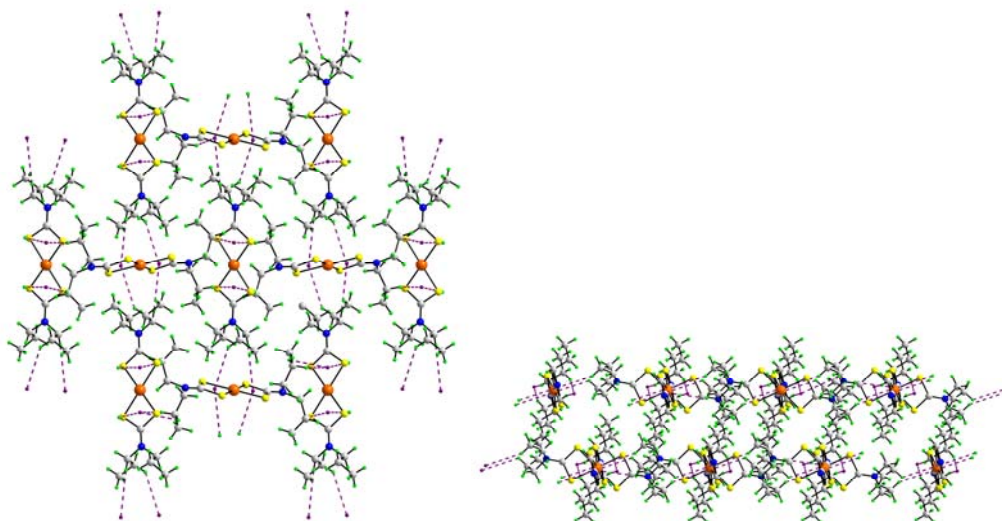
K. Ramalingam, K. Radha, G. Aravamudan, C. Mahadevan, C. Subramanyam, and M. Seshasayee, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 1838; CSD REF CODE: COKDOV.



C—H... π (PdS₂C) 3.07 Å; 156° & 3.11 Å; 119° & 3.26 Å; 141° & 3.38 Å; 156°

M.-L. Riekkola, T. Pakkanen, and L. Niinisto, *Acta Chem.Scand. A*, 1983, **37**, 807; CSD

REFCODE: COCWOG.

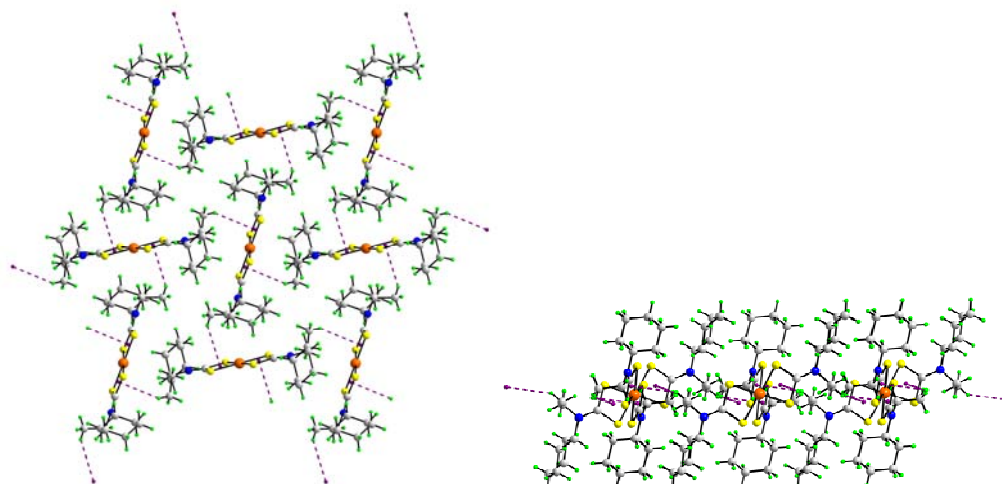


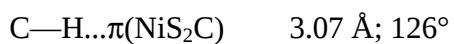
Ni[S₂CN(CH₂CH₃)Cy]₂

C—H... π (NiS₂C) 3.07 Å; 135°

M. J. Cox and E. R. T. Tiekink, *Z. Kristallogr.*, 1999, **214**, 242; CSD REFCODE:

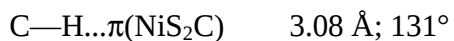
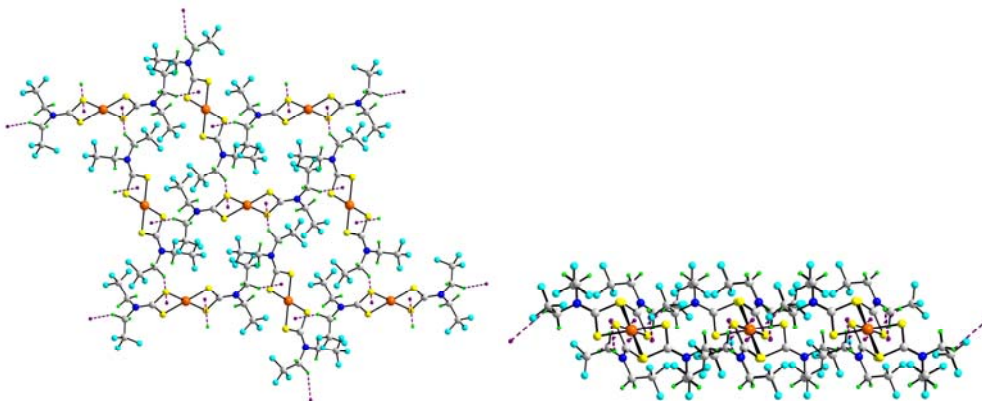
GOQYAM.



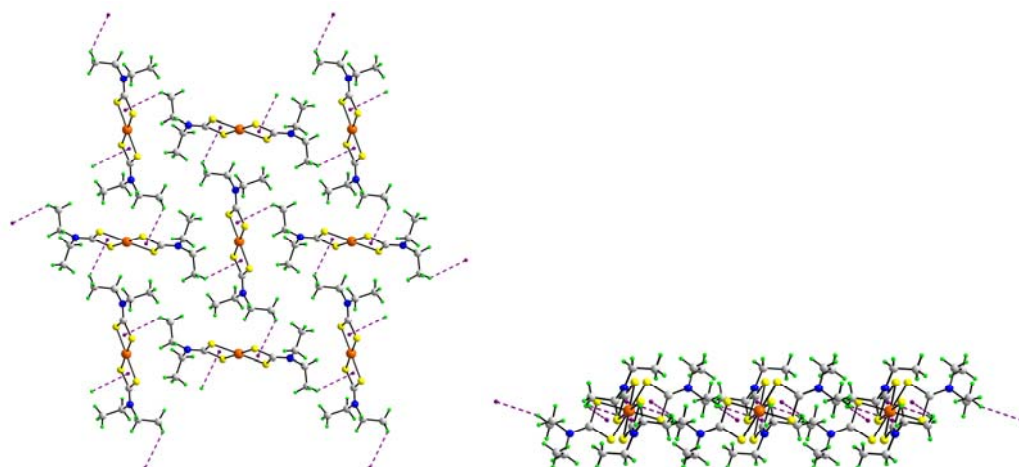


M. R. Sundberg and M.-L. Riekkola, *Inorg. Chim. Acta*, 1987, **132**, 99; CSD REFCODE:

FIDGEE. Isomorphous with COCXEX.



R. Selvaraju, K. Panchanatheswaran, A. Thiruvalluvar, and V. Parthasarathi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 606; M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, 1965, **19**, 619; CSD REFCODES: NIDCAR04/NIDCAR {3D coordinates are not available for NIDCAR01 & NIDCAR02}.

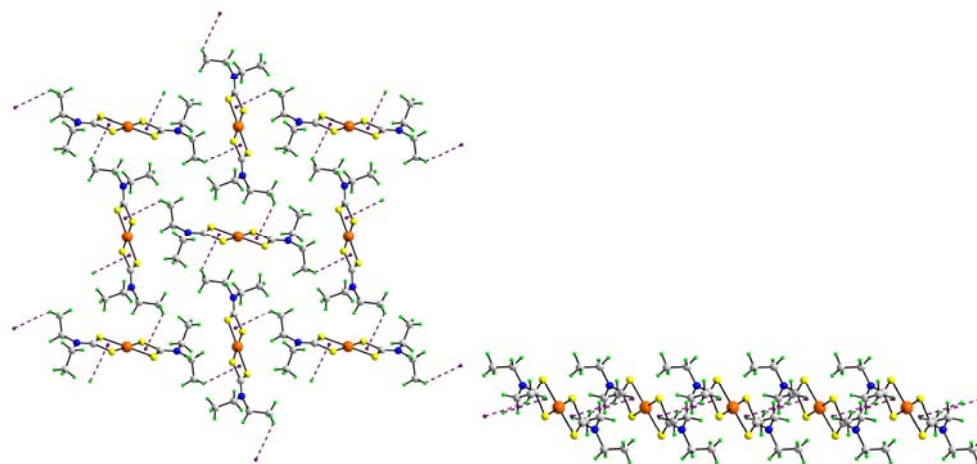


$\text{Mo}(\text{S}_2\text{CNEt}_2)_2$

$\text{C—H}\cdots\pi(\text{MoS}_2\text{C})$ 3.09 Å; 131°

G.-Y. He, F.-L. Bei, H.-Q. Chen, X.-Q. Sun, *J. Chem. Cryst.*, 2006, **36**, 481; CSD

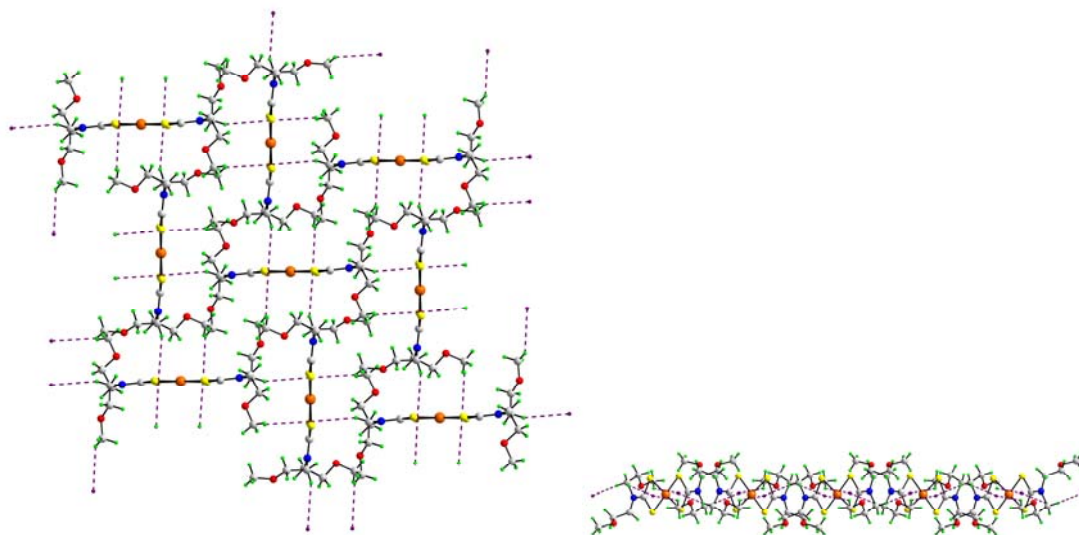
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$\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OCH}_3)_2]_2$

$\text{C—H}\cdots\pi(\text{NiS}_2\text{C})$ 3.11 Å; 131° & 3.24 Å; 158°

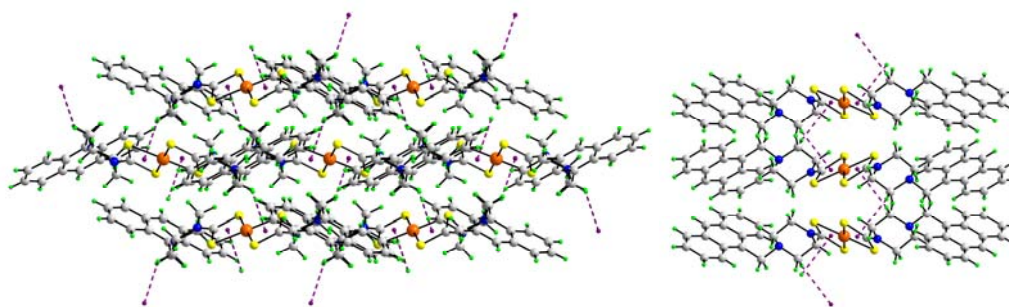
G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent, and I. Richards, *Inorg. Chim. Acta*, 2009, **362**, 1361; CSD REFCODE: SOTNOF.



$\text{Cu}\{\text{S}_2\text{C}[\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2(\text{anthracenyl})]\}_2$

$\text{C}\cdots\text{H}\cdots\pi(\text{CuS}_2\text{C})$ 3.11 Å; 128°

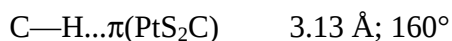
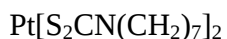
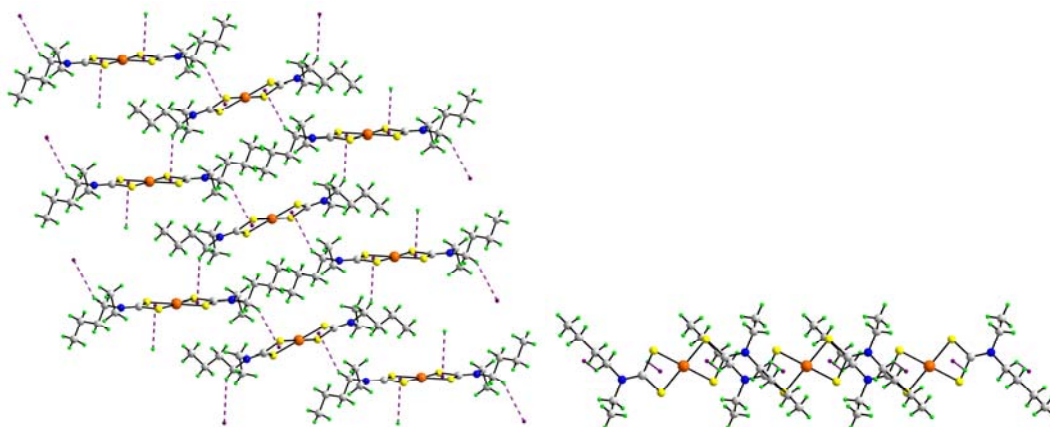
M. H. Lim and S. J. Lippard, *Inorg. Chem.*, 2006, **45**, 8980; CSD REFCODE: SEQQIP.



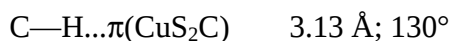
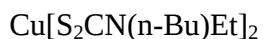
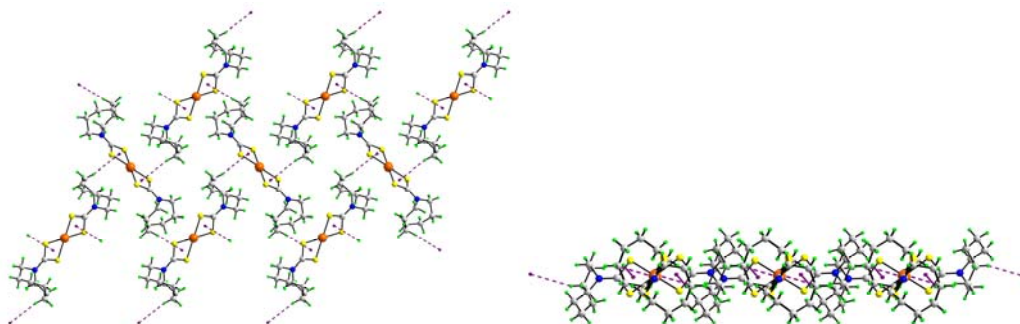
$\text{Ni}[\text{S}_2\text{CN}(\text{n-Bu})\text{Et}]_2$

$\text{C}\cdots\text{H}\cdots\pi(\text{NiS}_2\text{C})$ 3.12 Å; 131°

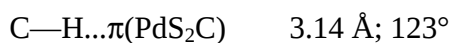
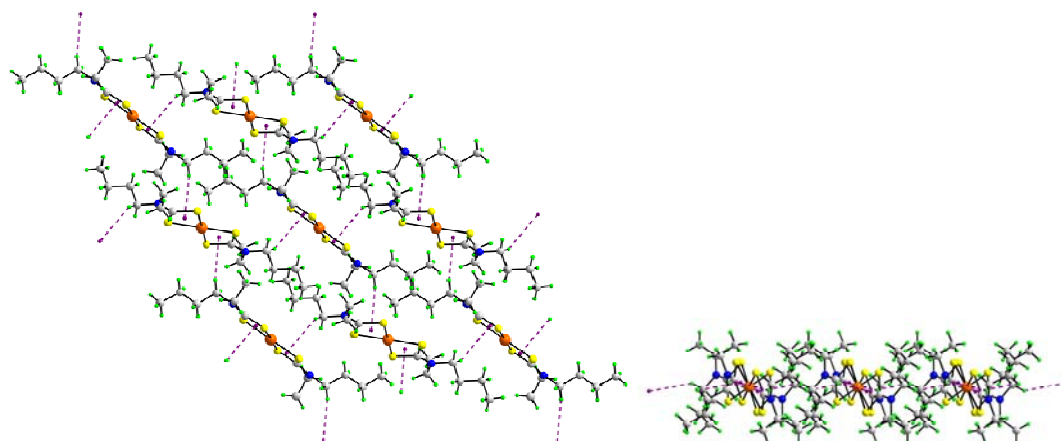
W. N. S. W. Juhari, I. Baba, Y. Farina, and S. W. Ng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, m339; CSD REFCODE: PUHVIIY. Isomorphous with UKEDOD.



G. A. Heath, D. C. R. Hockless, and P. D. Prenzler, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 537; CSD REFCODE: ZOZDOH.

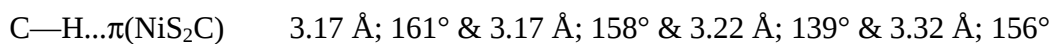
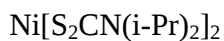
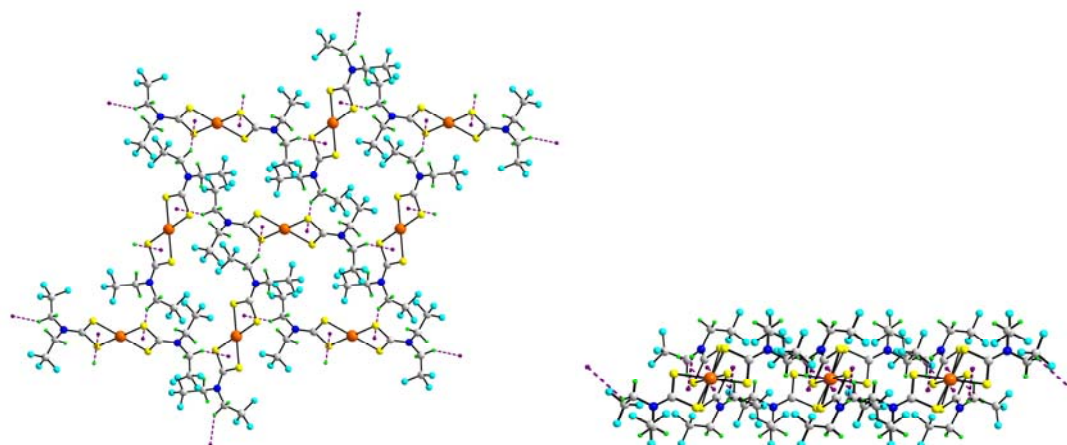


S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano, and J. T. Welch, *Polyhedron*, 2003, **22**, 1575; CSD REFCODE: UKEDOD. Isomorphous with PUHVIIY.



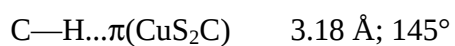
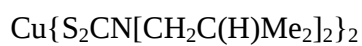
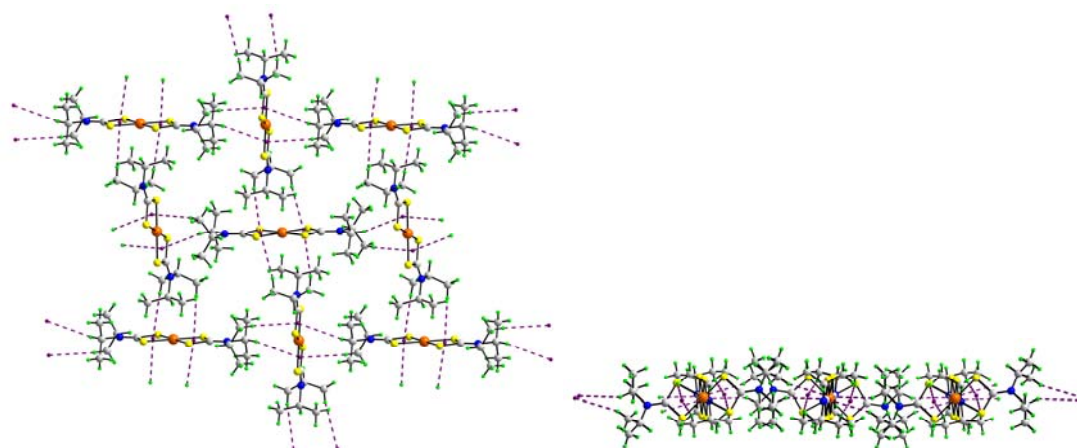
M.-L. Riekkola, T. Pakkanen, and L. Niinisto, *Acta Chem.Scand. A*, 1983, **37**, 807; CSD

REFCODE: COCXEX. Isomorphous with FIDGEE.

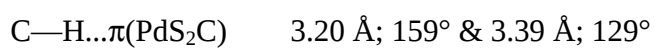
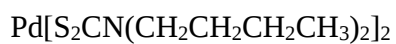
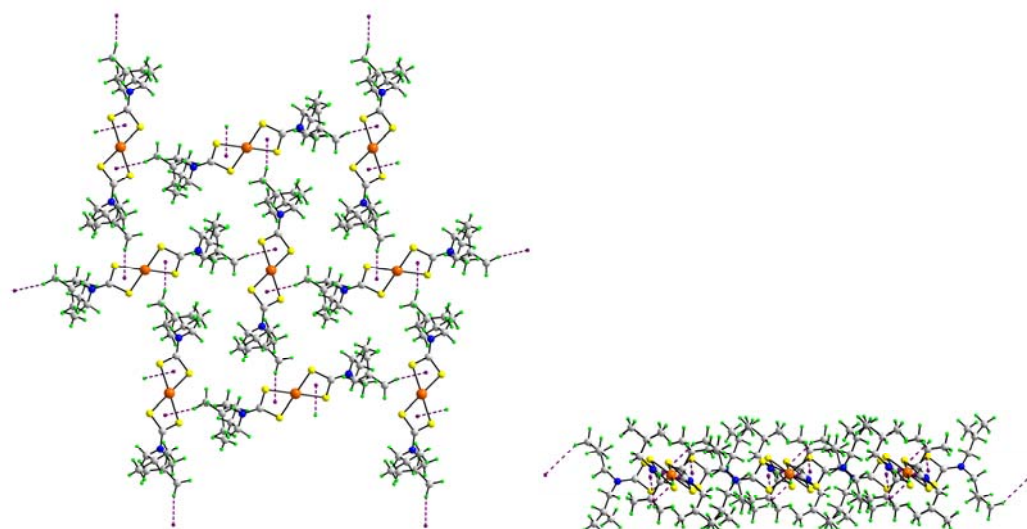


P. C. Healy, J. W. Connor, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1990, **43**,

1083; CSD REFCODE: IPTCNI10. Isomorphous with UFEWEH01.

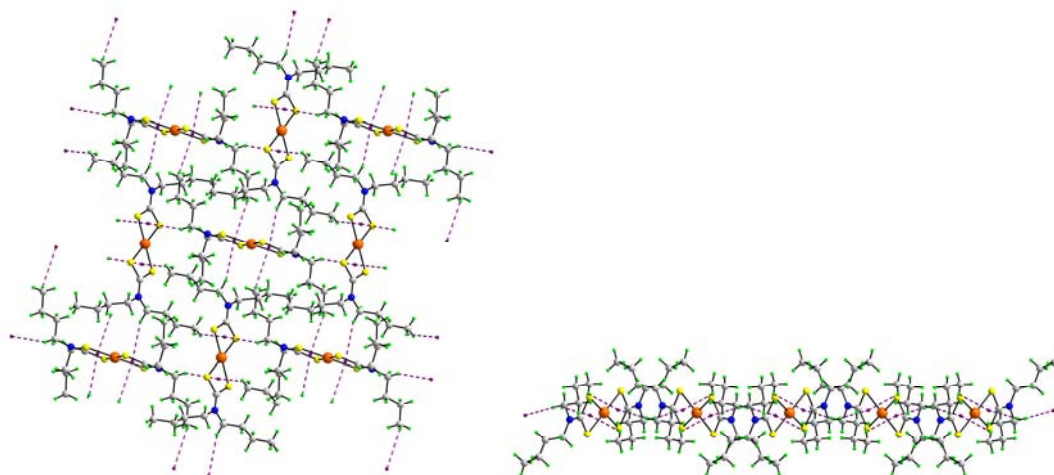


S. C. Ngo, K. K. Banger, M. J. DelaRosa, P. J. Toscano, and J. T. Welch, *Polyhedron*, 2003, **22**, 1575; CSD REFCODE: UKEDAP.



M.-L. Riekkola, T. Pakkanen, and L. Niinisto, *Acta Chem.Scand. A*, 1983, **37**, 807; CSD

REFCODE: COCWUM.

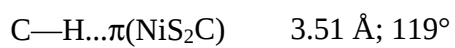
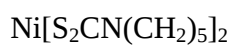
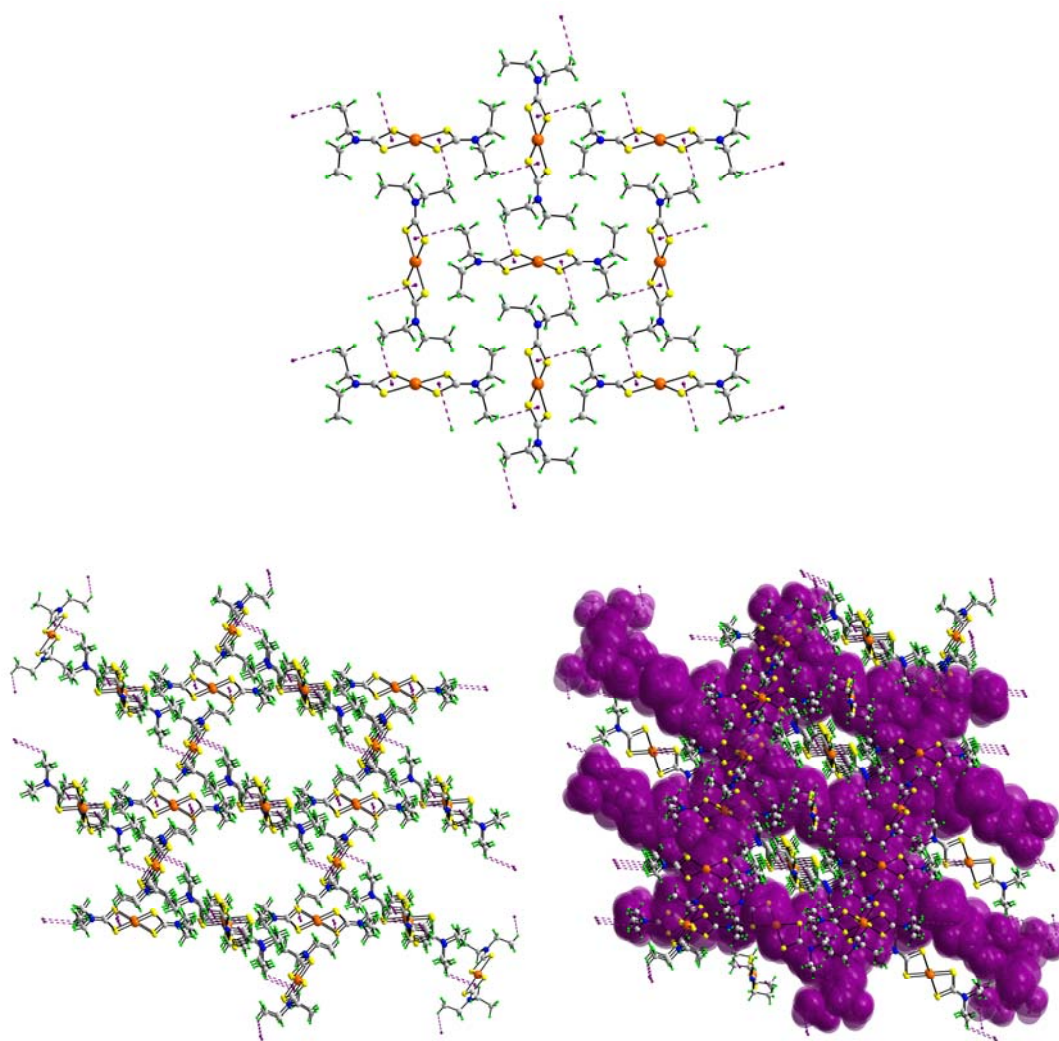


$\text{Pd}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2]_2$

$\text{C—H}\cdots\pi(\text{PdS}_2\text{C}) \quad 3.21 \text{ \AA}; 110^\circ$

P. P. Phadnis, V. K. Jain, T. Schurr, A. Klein, F. Lissner, T. Schleid, and W. Kaim, *Inorg. Chim. Acta*, 2005, **358**, 2609; F.-F. Jian, F. Bei, P. Zhao, X. Wang, H.-K. Fun, and K. Chinnakali, *J. Coord. Chem.*, 2002, **55**, 429; P. T. Beurskens, J. A. Cras, T. W. Hummelink, and J. H. Noordik, *J. Cryst. Mol. Struct.*, 1971, **1**, 253; CSD REFCODES: DETCPD02/DETC PD01/DETC PD.

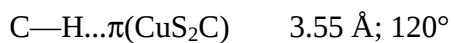
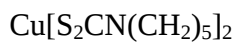
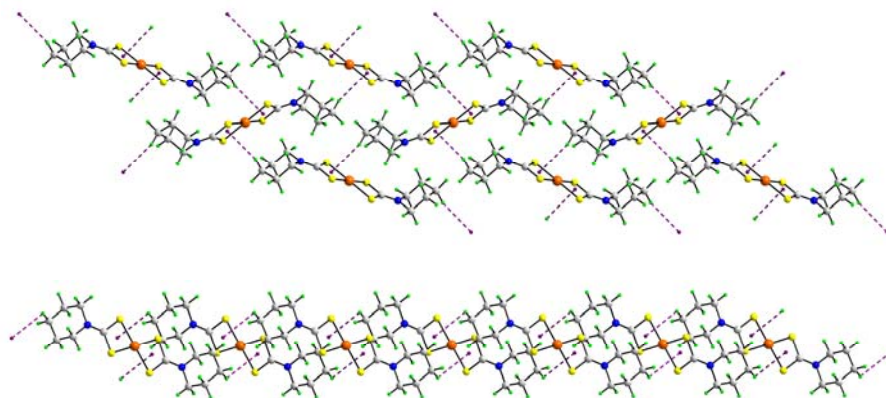
Two arrays mutually interpenetrate to complete the crystal packing.



V. Kettmann, J. Garaj, and S. Kudela, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1204;

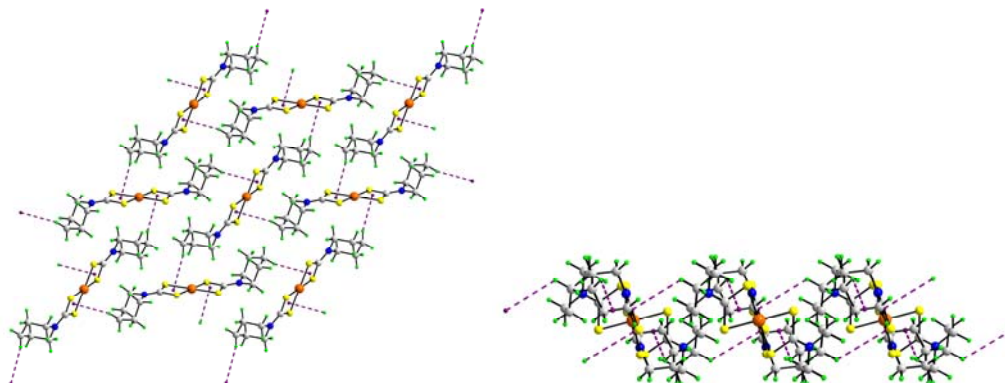
A. Radha, M. Seshasayee, and G. Aravamudan, *Acta Crystallogr., Sect. C: Cryst. Struct.*

Commun., 1988, **44**, 1378; CSD REFCODES: CPMXNI/CPMXNI01.

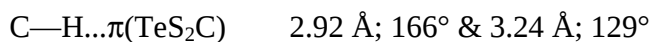


V. Kettmann, J. Garaj, and S. Kudela, *Collect. Czech. Chem. Commun.*, 1977, **42**, 402;

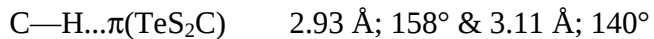
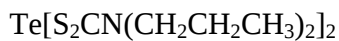
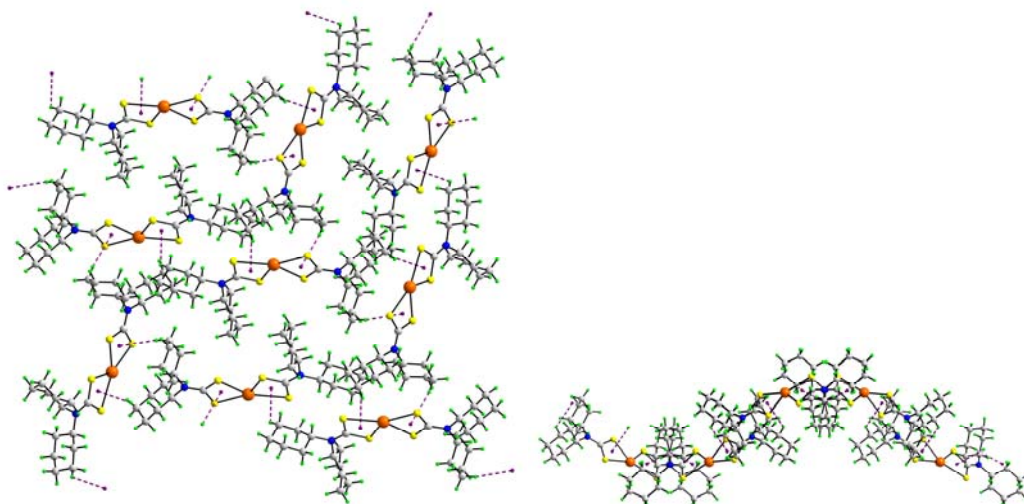
CSD REFCODE: PMTCCU. Hydrogen atom coordinates are not reported for PMTCCU01/ PMTCCU02/PMTCCU04.



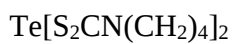
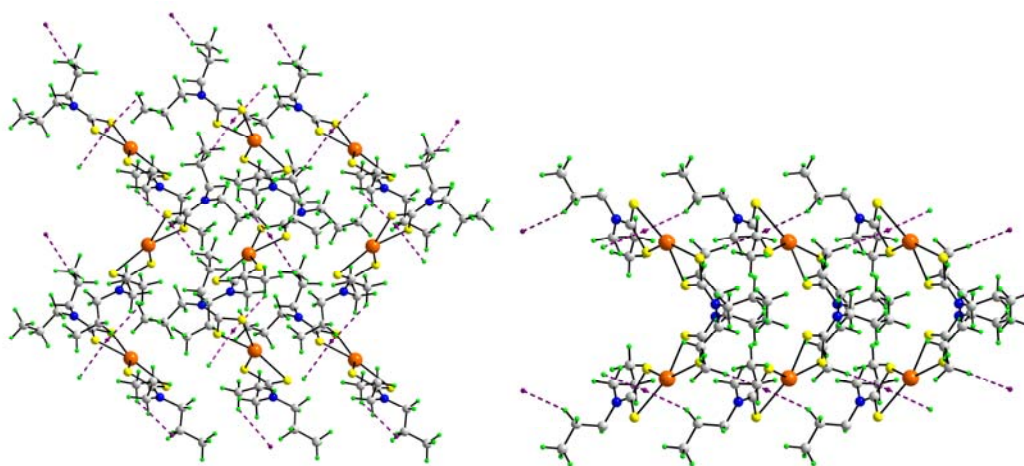
MAIN GROUP ELEMENT COMPOUNDS



M. J. Cox and E. R. T. Tiekink, *Z. Kristallogr.*, 1999, **214**, 584; CSD REFCODE:
LESQAB.

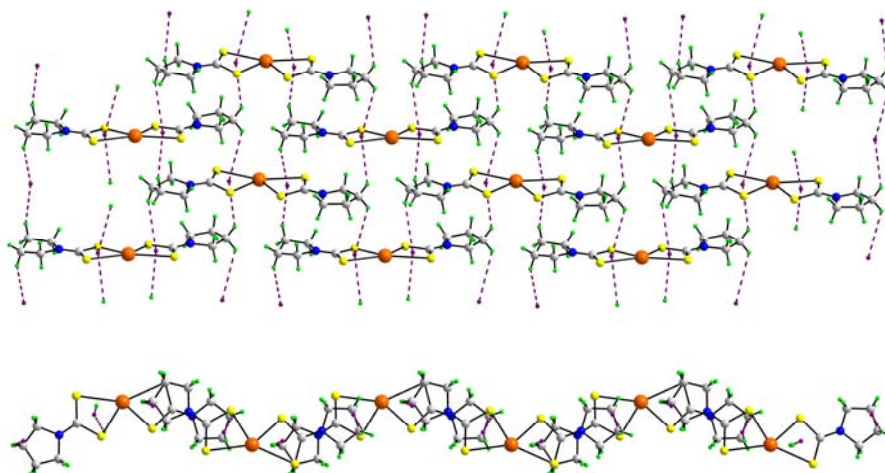


V. Ganesh, M. Seshasayee, Sp. Chidambaram, G. Aravamudan, K. Goubitz, and H. Schenk, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1506; CSD REFCODE: VASWAN.



C—H... π (TeS₂C) 2.98 Å; 152° & 3.20 Å; 146° & 3.21 Å; 139° & 3.44 Å; 129°

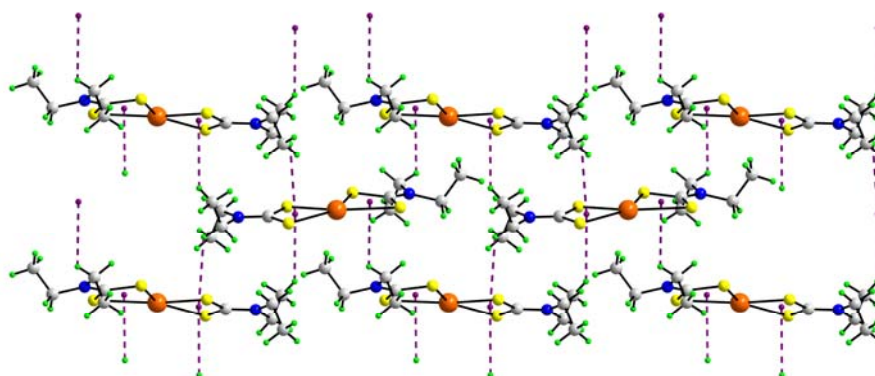
W. Tyrra, D. Naumann, S. Buslei, S. Kremer, I. Pantenburg, and H. Scherer, *Dalton*, 2007, 1829; CSD REFCODE: XICTIN.

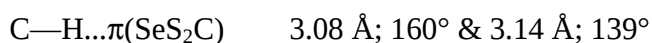
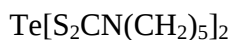
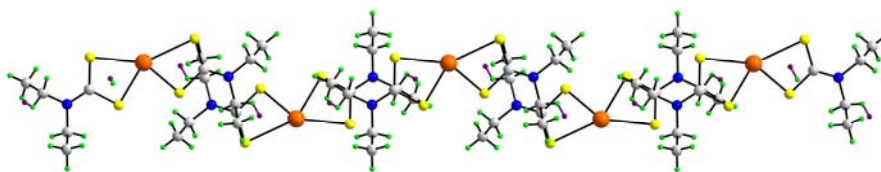


Te(S₂CNEt₂)₂

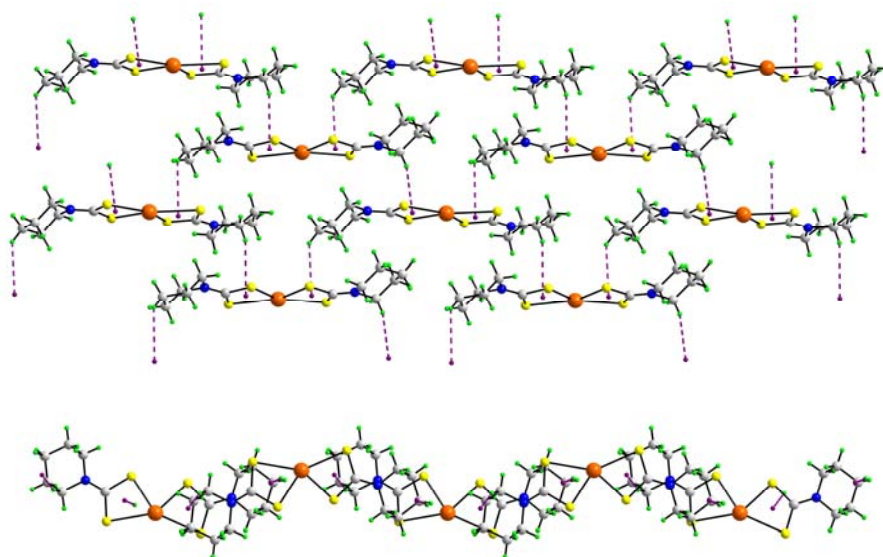
C—H... π (TeS₂C) 3.03 Å; 125° & 3.07 Å; 132° & 3.20 Å; 120°

C. Fabiani, R. Spagna, A. Vaciago, and L. Zambonelli, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **27**, 1499; CSD REFCODE: DETCTE.



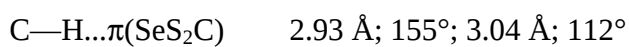


P. C. Srivastava, S. Bajpai, R. Lath, R. Kumar, V. Singh, S. Dwivedi, R. J. Butcher, S. Hayashi, and W. Nakanishi, *Polyhedron*, 2008, **27**, 835; CSD REFCODE: YISPEW; isostructural with SEBCAD.



MOTIF (V) – Solvent-mediated array

MAIN GROUP ELEMENT COMPOUND



T. M. Klapotke, B. Krumm, and M. Scherr, *Inorg. Chem.*, 2008, **47**, 4712; CSD

REFCODE: ROCHUN.

