A supramolecular synthon approach to aid the discovery of architectures sustained by C–H...M hydrogen bonds

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Electronic Supplementary Information

Table S(1). Diagrams and details of self-assembled zero-dimensional aggregates mediated by $\{...HCNNi\}_2$ synthons in molecular nickel complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

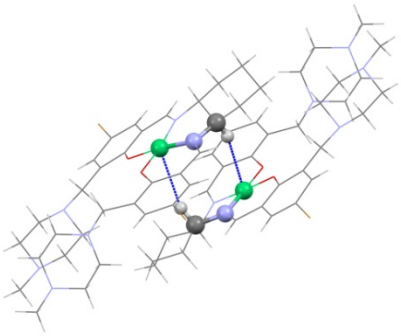
Table S(2). Diagrams and details of self-assembled supramolecular 1-D chains and 2-D layer mediated by $\{...HCNNi\}_2$ synthons in molecular nickel complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

Table S(3). Diagrams and details of self-assembled zero-dimensional aggregates mediated by $\{...HCNCu\}_2$ synthons in molecular copper complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

Table S(4). Diagrams and details of self-assembled supramolecular 1-D chains and 2-D layers mediated by $\{...HCNCu\}_2$ synthons in molecular copper complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

Figure S(1). Plots of distance, d (Å) versus angle, θ (°) for (a) nickel complexes and (b) copper complexes.

Table S(1). Diagrams and details of self-assembled zero-dimensional aggregates mediated by {...HCNNi}$_2$ synthons in molecular nickel complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.



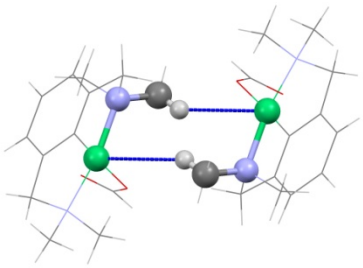
CEQVAW

bis(Oxonium) (N,N'-bis(5-bromo-3-(4-methylpiperazinylmethyl)salicylidene)-cyclohexane-1,2-diamine)-nickel(II) dichloride pentahydrate

M. Prabhakar, P. S. Zacharias and S. K. Das, *Inorg. Chem. Commun*, 2006, **9**, 899.

d = 2.55 Å, θ = 145°; d = 2.84 Å, θ = 154°.

Ionic (Ni cation) Schiff base with cyclohexyl bridge. Two molecules in the asymmetric unit which associate *via* methine-H.



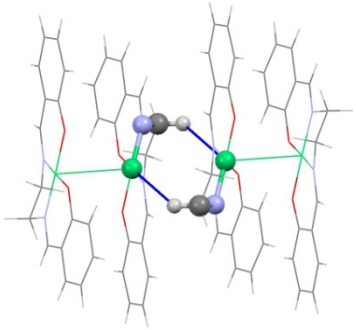
CESGAI10

Formato-(2,6-bis(dimethylaminomethyl)-phenyl-C,N,N')-nickel(II)

D. M. Grove, G. Van Koten, H. J. C. Ubble, R. Zoet and A. L. Spek, *Organometallics*, 1984, **3**, 1003.

d = 2.95 Å, θ = 149° {centre of inversion}.

Organometallic. Moelcules associate *via* N-CH_3.



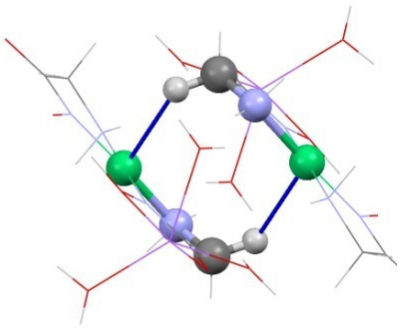
COXNIN

(N,N'-Ethylene-bis(salicylideneiminato))-nickel(II) dichloromethane solvate

M. A. Siegler and M. Lutz, *Cryst. Growth. Des*., 2009, **9**, 1194.

d = 2.95 Å, θ = 127° {centre of inversion}.

Schiff base with ethylene bridge. Molecules associate *via* methylene-H. Weak Ni...Ni interactions are noted which connect the dimeric aggregates into a linear supramolecular chain.

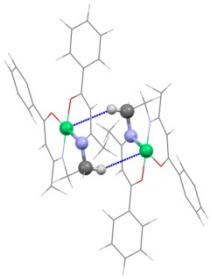


DABNID

Sodium bis(aminoacetohydroxamato-N,N')-nickel(II) trihydrate

M. J. Pouzol, S. Jaulmes, P. Laruelle, S. Carvalho and E. D. Paniago, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 712.

d = 2.87 Å, θ = 123° {centre of inversion}. Ionic (Ni anion) complex. Molecules associate *via* methylene-H. Weak Ni...Ni interactions are noted which connect the dimeric aggregates into a linear supramolecular chain.

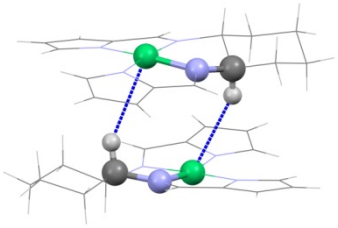


EBIMNI10

N,N'-Ethylene-bis(benzoylacetoniminato)-nickel(II)

V. Malatesta and A. Mugnoli, *Can. J. Chem.*, 1981, **59**, 2766.

d = 2.87 Å, θ = 146° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.



EDALIF & EDALIF01

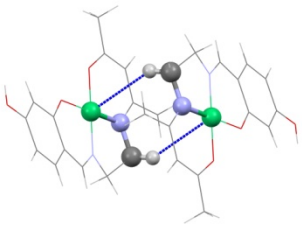
((1R,2R)-N1,N2-bis((Pyrrol-2-yl)methylene)cyclohexane-1,2-diamine)-nickel(II)

Y. Wang, H. Fu, F. Shen, X. Sheng, A. Peng, Z. Gu, H. Ma, J. S. Ma and J. Yao, *Inorg. Chem.*, 2007, **46**, 3548.

d = 2.82 Å, θ = 147°; *d* = 3.00 Å, θ = 148°.

X.-F. Shan, L.-Z. Wu, X.-Y. Liu, L.-P. Zhang and C.-H. Tung, *Eur. J. Inorg. Chem.*, 2007, 3315.

d = 2.81 Å, θ = 148°; *d* = 2.97 Å, θ = 148°. Schiff base with cyclohexyl bridge. Associate *via* methine-H. Four molecules in the asymmetric unit and two associate in this manner.

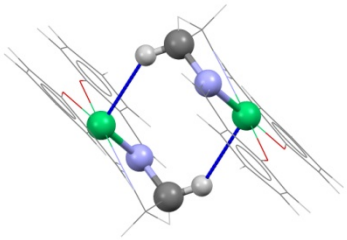


EXOBIC

(9-(2',4'-Dihydroxyphenyl)-5,8-diaza-4-methylnona-2,4,8-trienato)-nickel(ii) methanol solvate

N. T. S. Phan, D. H. Brown, H. Adams, S. E. Spey and P. Styring, *Dalton Trans*., 2004, 1348.

d = 2.99 Å, θ = 142° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* imine-C-methyl-H.

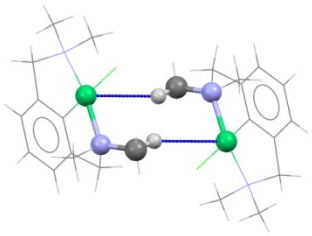


FEYWEM01 (monoclinic polymorph)

(N,N'-Ethylene-bis(salicylideneiminato))-nickel(II) chloroform solvate

M. A. Siegler and M. Lutz, *Cryst. Growth Des*., 2009, **9**, 1194.

d = 2.65 Å, θ = 138° {centre of inversion}. Schiff base with ethylene bridge. Associate *via* imine-C-methyl-H. The orthorhombic polymorph {**FEYWEM02**} also features this type of interaction but this part of the molecule is disordered so the structure has been discarded.

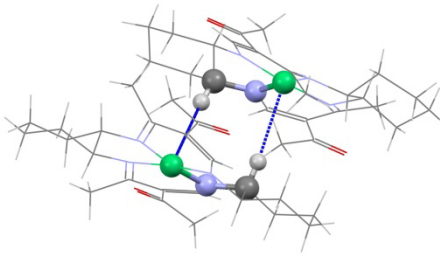


GAWNAU

(2,6-bis((Dimethylamino)methyl)phenyl-C,N,N')-chloro-nickel(II)

A. Castonguay, F. Charbonneau, A. L. Beauchamp and D. Zargarian, *Acta Crystallogr, Sect. E: Struct. Rep. Online*, 2005, **61**, m2240.

d = 2.96 Å, θ = 153° {centre of inversion}. Organometallic. Molecules associate *via* N-CH_3.

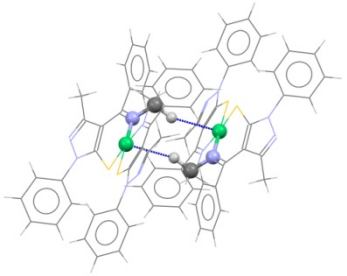


GUWROF

(7,16-Diacetyl-1,2,3,4,4a,9a,10,11,12,13,13a,18a-dodecahydro-5,9,14,18-tetra-azadibenzo(a,h)cyclotetradecenato)-nickel(II)

G. Du, A. Ellern and L. K. Woo, *Inorg. Chem.*, 2003, **42**, 873.

d = 2.89 Å, θ = 175°; d = 2.90 Å, θ = 174°. Macrocycle with two imine groups. Molecules associate *via* methine-H.

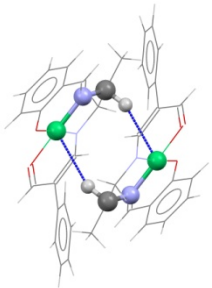


HADREK

(N,N'-bis(a-(5-Mercapto-3-methyl-1-phenylpyrazol-4-yl)benzylidene)ethane-1,2-diamine-N,N',S,S')-nickel(II)

H. Hennig, S. Knoblauch, B. Roland, M. Ecke, J. Sieler, S. Jelonek and F. Somoza, *Private Communication* to the CSD, 2003.

d = 2.66 Å, θ = 156° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

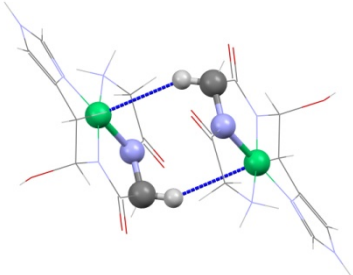


HAGXUI

(8-(2-Hydroxyphenyl)-6-methyl-1-oxo-2-phenyl-4,7-diazaocta-2,7-diene)-nickel(II) methanol solvate

I. M. Saez, G. H. Mehl, E. Sinn and P. Styring, *J. Organomet. Chem.*, 1998, **551**, 299.

d = 2.73 Å, θ = 157° {centre of inversion}. Imine-containing complex. Molecules associate *via* methine-H.

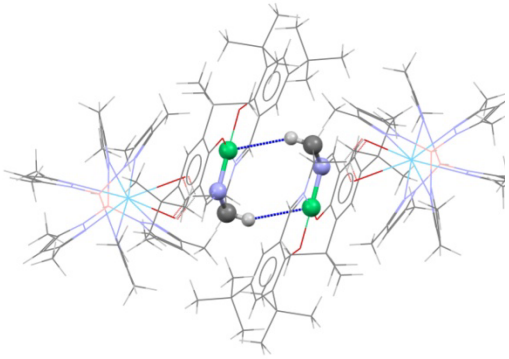


HERRIF

(Glycyl-glycyl-a-hydroxy-D,L-histamine)-nickel(II) trihydrate

W. Bal, M. I. Djuran, D. W. Margerum, E. T. Gray Jr, M. A. Mazid, R. T. Torn, E. Nieboer and P. J. Sadler, *Chem. Commun.*, 1994, 1889.

d = 2.88 Å, θ = 149° {centre of inversion} Molecules associate *via* amide-methylene-H.

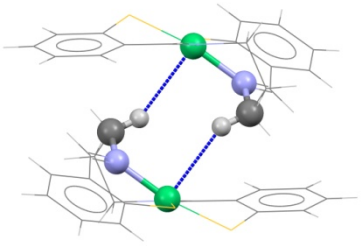


HURYAV

(μ_2-2,3-bis((3,5-di-t-butylsalicylidene)amino)propionato)-bis(hydrogen tris(3,5-dimethylpyrazol-1-yl)borate)-lanthanum-nickel hexane solvate

M. Schley, S. Fritzsche, P. Lonnecke and E. Hey-Hawkins, *Dalton Trans*. 2010, **39**, 4090.

d = 2.77 Å, θ = 148° {centre of inversion}. Heterometallic (La) complex with Schiff base with (carboxylate)ethylene bridge. Molecules associate *via* methylene-H.

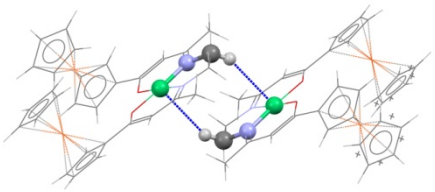


IWOYOI

(N,N'-Bis-(o-sulfidobenzylidene)-1,3-diaminopropane)nickel(II) 1,4-dioxane solvate

M. K. Taylor, J. Reglinski and D. Wallace, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2004, **60**, m850.

d = 2.80 Å, θ = 145° {centre of inversion}. Schiff base with propylene bridge. Molecules associate *via* α-methylene-H.

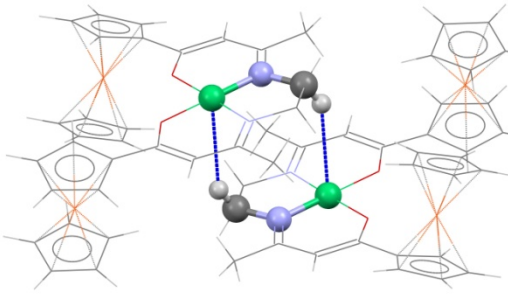


IXOCON (*P*2$_1$/*n* monoclinic polymorph)

(N,N'-Ethylene-bis(ferrocenoylacetoiminato))-nickel(II)

Y-.C. Shi, W-.B. Shen, H-.M. Yang, H-.B. Song and X-.Y. Hu, *Polyhedron*, 2004, **23**, 749.

d = 2.95 Å, θ = 146° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

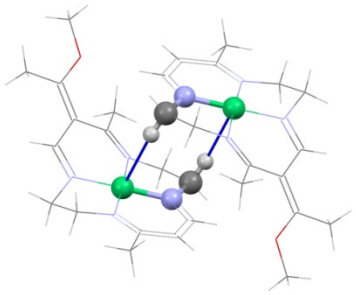


IXOCON01 (*C*2/*c* monoclinic polymorph)

(N,N'-Ethylene-bis(ferrocenoylacetoiminato))-nickel(II)

M. Fuentealba, M. T. Garland, D. Carrillo, C. Manzur, J. –R. Hamon and J.-Y. Saillard, *Dalton Trans*., 2008, 77.

d = 2.90 Å, θ = 140° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

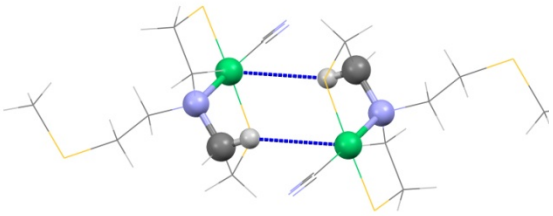


JEZTUD

(2,9-Dimethyl-3-(1-methoxyethylidene)-1,5,8,12-tetra-azacyclotetradec-1,4,9,11-tetraenato)-nickel(II) hexafluorophosphate

C. P. Horwitz, R. Navarro and G. C. Dailey, *Inorg. Chem*., 1990, **29**, 4262

d = 2.76 Å, θ = 159° {centre of inversion}. Macrocyclic with imine groups. Molecules associate *via* methylene-H.

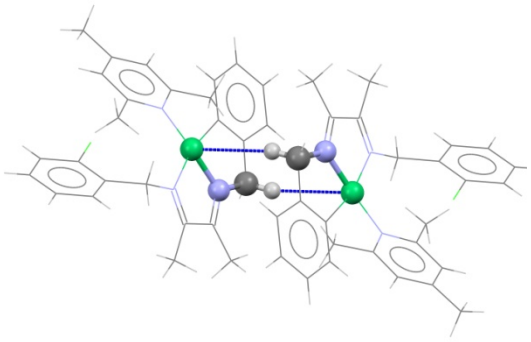


JUXZOR

Tetraethylammonium cyano-(N,N-bis(2-mercaptoethyl)-2-(methylthio)ethylamine)-nickel(II)

S. A. Mirza, M. A. Pressler, M. Kumar, R. O. Day and M. J. Maroney, *Inorg. Chem*., 1993, **32**, 977.

d = 2.93 Å, θ = 155° {centre of inversion}. Ionic (Ni anion) organometallic tertiary amine complex. Molecules associate *via* amine-α-methylene-H.

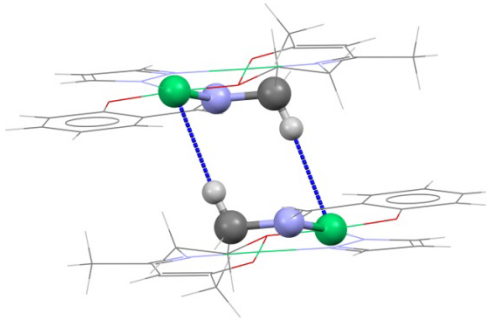


KAFPUD

(2,4,6-trimethylpyridine)-(2-((3-(N-2-chlorobenzyl)iminobut-2ylidene)aminomethyl)-phenyl)-nickel tetrafluoroborate

R. M. Cedre, G. Muller, M. Ordinas, M. Font-Bardia and X. Solans, *Dalton Trans*., 2003, 3052.

d = 2.91 Å, θ = 167° {centre of inversion}. Ionic (Ni cation) organometallic complex. Molecules associate *via* imine-methylene-H.

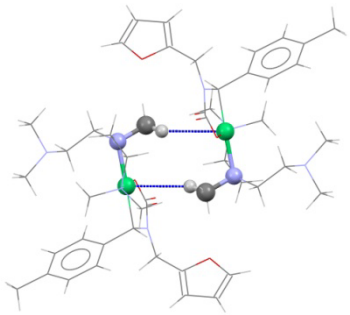


LEYVOA

(μ_2-N-(3-(Acetylacetonimino)-propyl-2-olato)salicylideneimine)-(μ_2-pyrazolato)-di-nickel(II)

P. E. Kruger, B. Moubaraki, K. S. Murray and E. R. T. Tiekink, *J. Chem. Soc. Dalton Trans*., 1994, 2129.

d = 2.83 Å, θ = 163° {centre of inversion}. Binuclear molecule with one nickel centre forming an interaction, *via* imine-methylene-H.

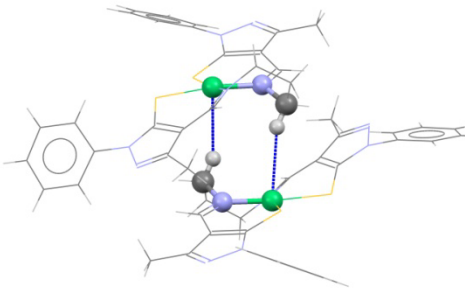


MIYRAN

(N,N,N',N'',N''-Pentamethyldiethylenetriamine-N,N')-(a-(N-carboxylato-N-(furfuryl)amino)-4-methylbenzyl-C,O)-nickel(II) tetrahydrofuran solvate

D. Walther, R. Kilian, H. Schreer and H. Gorls, *Z. Anorg. Allg. Chem*., 2002, **628**, 851.

d = 2.89 Å, θ = 127° {centre of inversion}. Organometallic tertiary amine complex. Molecules associate *via* amine-methyl-H.

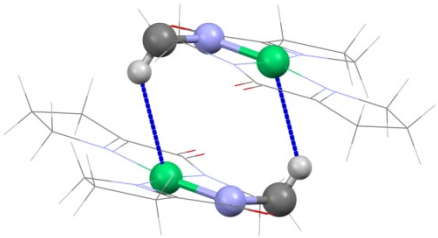


NEKFIS

(N,N'-bis(5-Mercapto-3-methyl-1-phenylpyrazol-4-ylmethylene)propane-1,3-diamine)-nickel(II)

B. Adhikari, O. P. Anderson, A. La Cour, R. Hazell, S. M. Miller, C. E. Olsen and H. Toftlund, *J. Chem. Soc. Dalton Trans*., 1997, 4539.

d = 2.80 Å, θ = 154°; *d* = 2.81 Å, θ = 149°. Schiff base with propylene bridge. Two independent molecules and these associate *via* α-methylene-H.

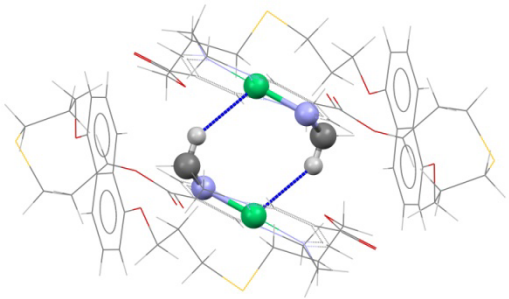


OFAFOQ

(N,N'-bis(1-Pyrrolin-2-ylcarbonyl)ethylenediamine-N,N',N'',N''')-nickel(II) monohydrate

C. L. Weeks, P. Turner, R. R. Fenton, P. A. Lay, J. Chem. Soc. Dalton Trans, 2002, 931.

d = 2.89 Å, θ = 134° {centre of inversion}. Ethylenediamine derivative. Molecules associate *via* N-methylene-H.

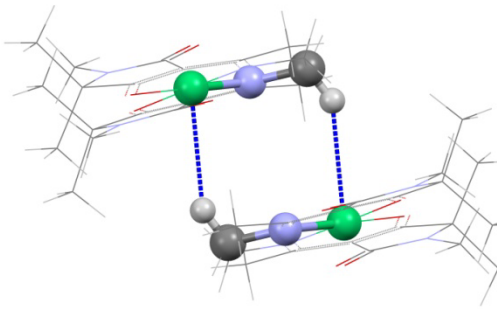


ONUGAG

[13,16,110,113-tetraaza-3,11,13,21-tetraoxa-2,22-dioxo-7,17-dithia-1(1,8)-cyclotetradecana-12(1,5)-naphtalenadocosacyclophano-11,16,18,113-tetraenato]-nickel(II)

R. Kaminski, J. Kowalski, I. Manes, B. Korybut-Daszkiewicz, S. Domagala and K. Wozniak, *Eur. J. Inorg. Chem*., 2011, 479.

d = 2.56 Å, θ = 144° {centre of inversion}. Macrocyclic imine groups. Molecules associate *via* methylene-H.

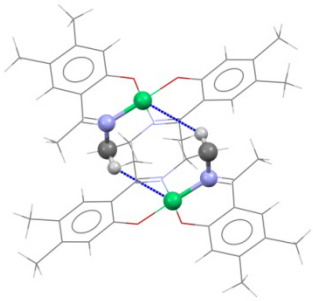


PANNEX

N,N'-Ethylene-bis(1',5',5'-trimethylpyrrolidin-2',4'-dion-3'-acetiminato)-nickel(II) hemihydrate

A. Zschunke, U. Botter, R. Donau, H. Bogge, A. Muller, A. Hauser and R. Luck, *Z. Anorg. Allg. Chem.*, 1992, **614**, 87.

d = 2.85 Å, θ = 147° {centre of inversion}. Schiff base with ethylene bridge. Two independent molecules and one of these self-associates *via* methylene-H.

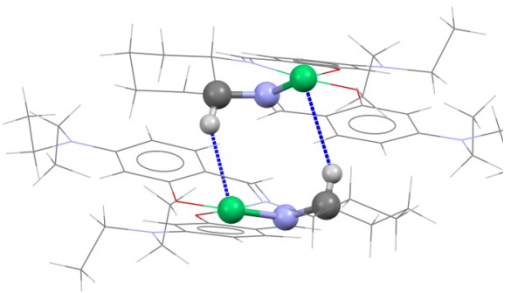


POFBAO

(4,4',5,5'-Tetramethyl-2,2'-(1,1'-(ethane-1,2-diyldinitrilo)diethylidyne)diphenolato)-nickel(II) chloroform methanol solvate

H-.K. Fun and R. Kia, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2008, **64**, m1116.

d = 2.99 Å, θ = 139° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

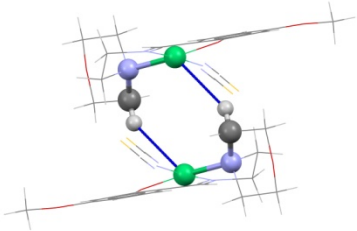


POYPEY

(1,2-bis(4-(Diethylamino)salicyaldiminato)cyclohexane)-nickel(II) ethanol solvate

G. Lenoble, P. G. Lacroix, J. C. Daran, S. Di Bella and K. Nakatani, *Inorg. Chem.*, 1998, **37**, 2158.

d = 2.60 Å, θ = 149°; d = 3.00 Å, θ = 146°. Schiff base with cyclohexyl bridge. Two independent molecules and these associate *via* methine-H.

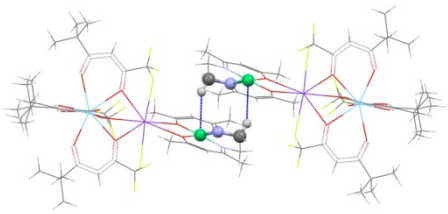


PUHMIP

(5-Methoxy-2-(((2-(morpholin-4-yl)ethyl)imino)methyl)phenolato)-thiocyanato-nickel(II)

L. Li, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, m289.

d = 2.97 Å, θ = 151° {centre of inversion}. Tertiary amine complex. Molecules associate *via* methylene-H.

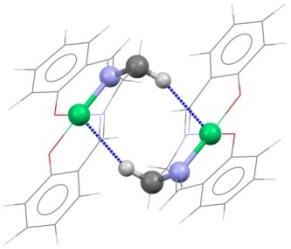


QEZYID

tris(μ_2-1,1,1-trifluoro-5,5-dimethyl-hexane-2,4-dionato)-(1,1,1-trifluoro-5,5-dimethyl-hexane-2,4-dionato)-(μ_2-N,N'-bis(4-oxypent-3-ene-2-ylidene)ethane-1,2-diamine-N,N',O,O')-lanthanum(III)-nickel(II)-potassium

N. Kuzmina, M. Ryazanov, I. Malkerova, A. Alikhanyan and A. N. Gleizes, *Eur. J. Inorg. Chem.*, 2001, 701.

d = 2.79 Å, θ = 146° {centre of inversion}. Ionic heterometallic (La; neutral Ni) complex. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.



SAENNI & SAENNI01-06 (redeterminations)

(N,N'-Ethylene-bis(salicylideneiminato))-nickel(II)

L. M. Shkol'nikova, E. M. Yumal, E. A. Shugam and V. A. Voblikova, *Zh. Strukt. Khim.*, 1970, **11**, 886.

d = 2.62 Å, θ = 155° {centre of inversion}.

A. G. Manfredotti and C. Guastini, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun*, 1983, **39**, 863.

d = 2.61 Å, θ = 153° {centre of inversion}

E. F. DiMauro and M. C. Kozlowski, *Organometallics*, 2002, **21**, 1454.

d = 2.73 Å, θ = 154° {centre of inversion}

M. Kondo, K. Nabari, T. Horiba, Y. Irie, Md. K. Kabir, R. P. Sarekr, E. Shimizu, Y. Shimizu and Y. Fuwa, *Inorg. Chem. Commun.*, 2003, **6**, 154.

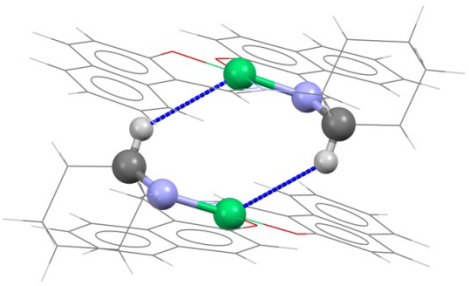
d = 2.75 Å, θ = 155° {centre of inversion}

M. A. Sieglre and M. Lutz, *Cryst. Growth, Des.*, 2009, **9**, 1194.

d = 2.67 Å, θ = 154° {centre of inversion}

Y. Ding, F. Wang, L. S. Wang and Q. R. Wang, *Koord. Khim.*, 2009, **35**, 366.

d = 2.73 Å, θ = 155° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.



SORHAJ (*cf.* methanol solvate SORHEN)

(1,1'-(1,2-cyclohexanediylbis((nitrilo)methylidene))di(2-naphtholato))-nickel(II) monohydrate

R. H. Hul and P. Zhou, *Synth. React. Inorg. Mat. Org. Nano-Met. Chem.*, 2007, **37**, 643.

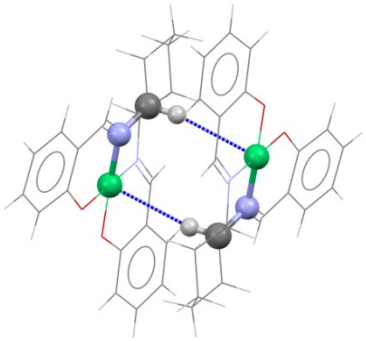
Four independent molecules

d = 2.96 Å, θ = 156° {centre of inversion}

d = 2.91 Å, θ = 136° {centre of inversion}

d = 2.89 Å, θ = 132°; d = 2.93 Å, θ = 133°.

Schiff base with cyclohexyl bridge. There are four independent molecules and all associate *via* methine-H.

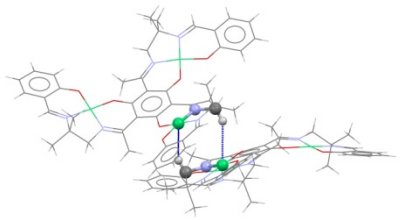


SORHEN (*cf.* water solvate, SORHAJ)

(1,1'-(1,2-cyclohexanediylbis((nitrilo)methylidene))diphenolato)-nickel(II) methanol solvate

R. H. Hul and P. Zhou, *Synth. React. Inorg. Mat. Org. Nano-Met. Chem.*, 2007, **37**, 643.

d = 2.88 Å, θ = 161° {centre of inversion}. Schiff base with cyclohexyl bridge. Molecules associate *via* methine-H.

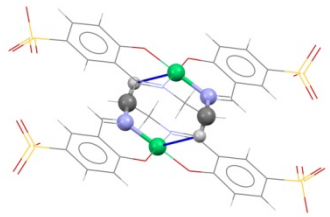


TAGHEP

(μ_3-1,3,5-tris(1-(2-Salicylaldimino-2-methylpropylimino)ethyl)benzene-2,4,6-triolato)-tri-nickel(II) chloroform toluene solvate

T. Glaser, M. Heidemeier and T. Lugger, *Dalton Trans.*, 2003, 2381.

d = 2.95 Å, θ = 148° {two-fold axis}. Trinuclear Schiff base complex with (methyl)ethylene bridge. Molecules associate *via* methylene-H between one of the independent Ni centres.

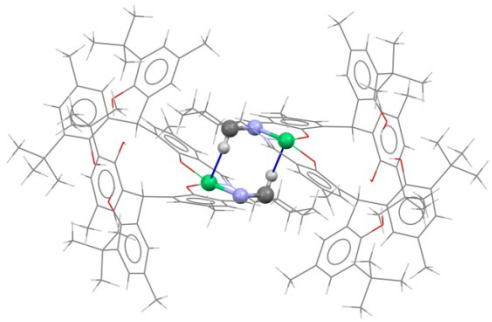


TAHDAJ

Sodium hydroxonium (N,N'-bis(5-sulfonatosalicylidene)ethane-1,2-diamine)-nickel hydrate

E. Delahaye, M. Diop, R. Welter, M. Boero, C. Massobrio, P. Rabu and G. Rogez, *Eur. J. Inorg. Chem*., 2010, 4450.

d = 2.98 Å, θ = 124° {centre of inversion}. Ionic (Ni anion) Schiff base complex with ethylene bridge. Associate *via* methylene-H. Although a polymeric architecture, the structure is classified as zero-dimensional as the $\{\ldots HCNNi\}_2$ synthons only connect two species.

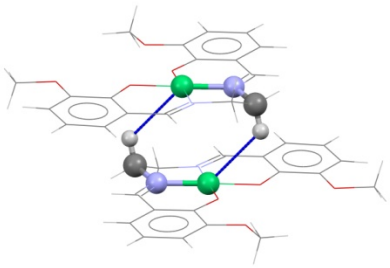


TEFWEH

(2,2',2'',2'''-(Cyclohexane-1,2-diylbis(nitrilomethylidene(2-oxy-5-methyl-3,1-phenylene)methanetriyl))tetrakis(6-t-butyl-4-methylphenol)-N,N',O,O')-nickel(II) tetra-n-butylammonium fluoride diethyl ether solvate

E. R. Libra and M. J. Scott, *Chem. Commun*., 2006, 1485.

d = 2.82 Å, θ = 129° {centre of inversion}. Schiff base with cyclohexyl bridge. Molecules associate *via* methine-H.

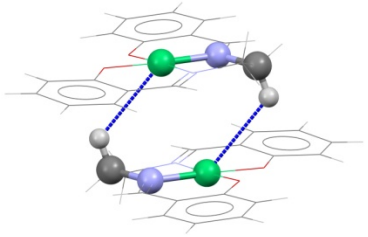


ULAMIE

(6,6'-Dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethanylidene)]diphenolato)-nickel(II) dimethylformamide solvate

K. Ayikoe, R. J. Butcher and Y. Gultnesh, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2011, **67**, m328.

d = 2.94 Å, θ = 125° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

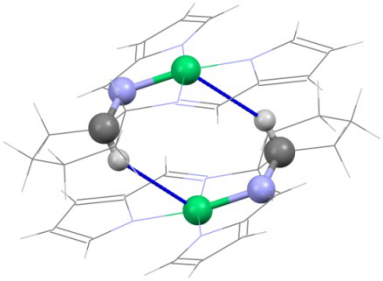


UMIBAT

(N,N'-Ethylene-bis(salicylideneiminato-N,O))-nickel(II) dimethylformamide solvate

M. Lutz, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, m950.

d = 2.92 Å, θ = 122° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

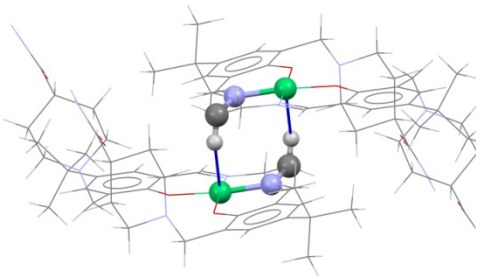


VIDKAV01

(N,N'-bis(Pyrrol-2-ylmethylene)cyclohexane-1,2-diamine-N,N',N'',N''')-nickel(II)

X.F. Shan, L.Z. Wu, X.Y. Liu, L.P. Zhang, C.H. Tung, Eur. J. Inorg. Chem. 2007, 3315.

d = 2.88 Å, θ = 142° {centre of inversion}. Schiff base with cyclohexyl bridge. There are two independent molecules and one of these self-associates *via* methine-H.



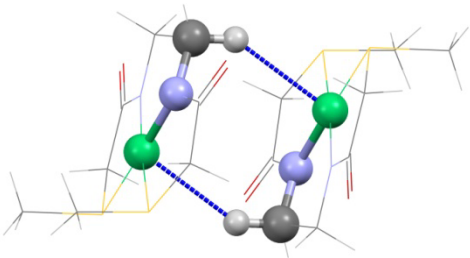
VIHDUM

(N,N'-bis(5-t-Butyl-3-(4-(carbamoyl)piperidylmethyl)salicylidenato)eth

ane-1,2-diamine-N,N',O,O')-nickel(II) chloroform diethyl ether solvate

S. G. Galbraith, Q. Wang, L. Li, A. J. Bake, C. Wilson, S. F. Collinson, J. F. Lindoy, P. G. Plieger, M. Schröder and P. A. Tasker, *Chem. Eur. J.*, 2007, **13**, 6091.

d = 2.88 Å, θ = 137° {centre of inversion}. Schiff base with ethylene bridge. There are three independent molecules and one of these self-associates *via* methylene-H.

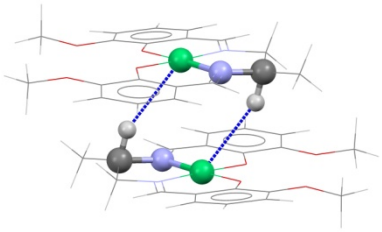


WARKEG

(N,N'-ethylenebis(2-methylmercaptoacetamide))-nickel(II)

O. Hatlevik, M. C. Blanksma, V. Mathrubootham, S. M. Arif and E. L. Hegg, *J. Biol. Inorg. Chem.*, 2004, **9**, 238.

d = 2.71 Å, θ = 146° {centre of inversion}. Ethylenediamine derivative. Molecules associate *via* methylene-H.

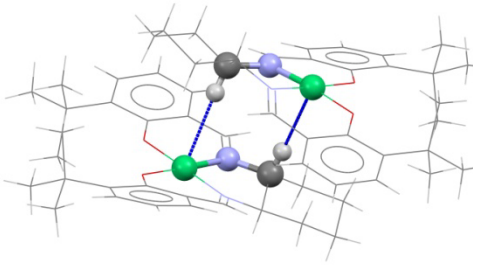


WAVYIB

(N,N'-bis(3-Methoxysalicylidene)propane-1,2-diamine-O,O',N,N')-nickel(II) aqua-dichloro-dimethyl-tin(IV)

D. Cunningham, J. F. Gallagher, T. Higgins, P. McArdle, J. McGinley, M. O'Gara, *J. Chem. Soc. Dalton Trans*., 1993, 2183.

d = 2.87 Å, θ = 152° {centre of inversion}. Schiff base with (methyl)ethylene bridge. Molecules associate *via* methine-H.

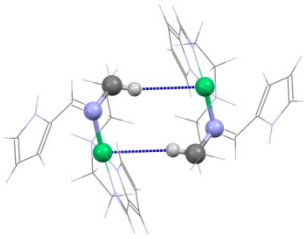


XUMBOW

(R,R)-(N,N'-bis(3-t-butylsalicylidene)-1,2-cyclohexanediamino)-nickel(II)

D. Vanderveer, M. L. Colon and X. R. Bu, 2002, *Anal. Sci.*, **18**, 1283.

d = 2.62 Å, θ = 174°; *d* = 2.63 Å, θ = 177°. Schiff base with cyclohexyl bridge. There are two independent molecules and these associate *via* methine-H.

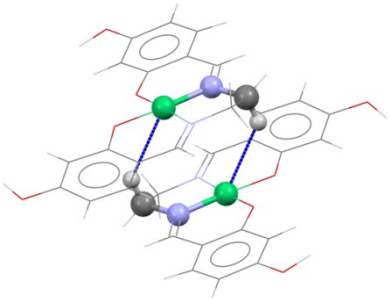


YAXFEI

1-(2-Pyrrolyl)-10-(pyrrol-1,2-diyl)-2,6,9-triazaundeca-1,9-diene-nickel(II) perchlorate

E. Kwiatkowski, M. Kwiatkowski, A. Olechnowicz and G. Bandoli, *J. Crystallogr. Spectrosc. Res*., 1993, **23**, 473.

d = 2.94 Å, θ = 159° {centre of inversion}. Imine derivative with ethylene bridge to amine. Molecules associate *via* methylene-H.



YELPUB

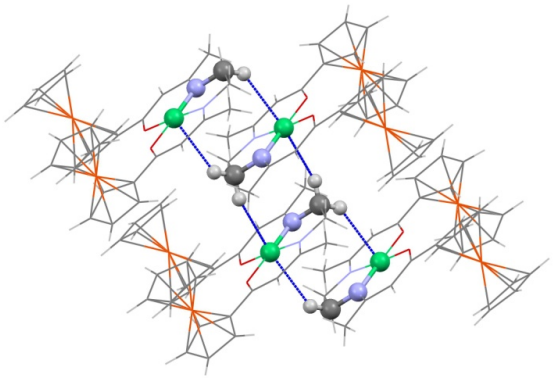
(N,N'-Ethylenebis(4-hydroxysalicylideneiminato))-nickel(II) dimethylformamide solvate

Y. Abe, H. Akao, Y. Yoshida, H. Takashima, T. Tanase, H. Mukai and K. Ohta, *Inorg. Chim. Acta*, 2006, **359**, 3147.

d = 2.77 Å, θ = 133°{centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* methylene-H.

Table S(2). Diagrams and details of self-assembled supramolecular 1-D chains and 2-D layer mediated by {...HCNNi}$_2$ synthons in molecular nickel complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

ONE-DIMENSIONAL CHAINS

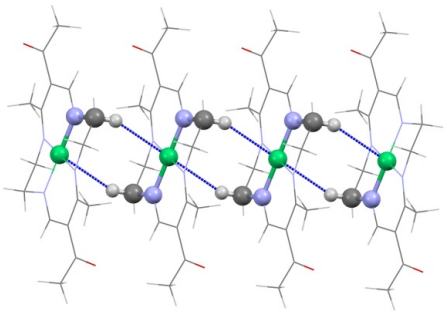


CERZIJ

(1,1'-Diferrocenyl-3,3'-(ethane-1,2-diyldinitrilo)dibutanolato)-nickel(II) dichloromethane solvate

P. D. W. Boyd, P. M. Johns and C. E. F. Rickard, *Acta Crystallogr. Sect. E: Struct. Rep. Online,* 2006, **62**, m3260.

d = 2.68 Å, θ = 154°; d = 2.79 Å, θ = 134°. Schiff base complex with ethylene bridge. Each methylene-H atom of a single methylene group forms an interaction leading to a linear supramolecular chain.

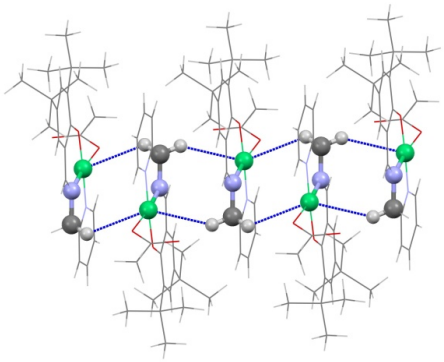


DETZIM

(6,13-bis(Acetyl)-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene)-nickel(II) dihydrate

A. Rybka, R.Kolinski, J. Kowalski, R. Szmigielski, S. Domagala, K. Wozinak, S. Wieckpwska, R. Bilewicz and B. K. Daszkiewicz, *Eur. J. Inorg. Chem*., 2007, 172.

d = 2.78 Å, θ = 154° {centre of inversion}. Centrosymmetric macrocycle with two imine groups. Centrosymmetrically related methylene-H atoms form the interactions leading to a linear supramolecular chain.

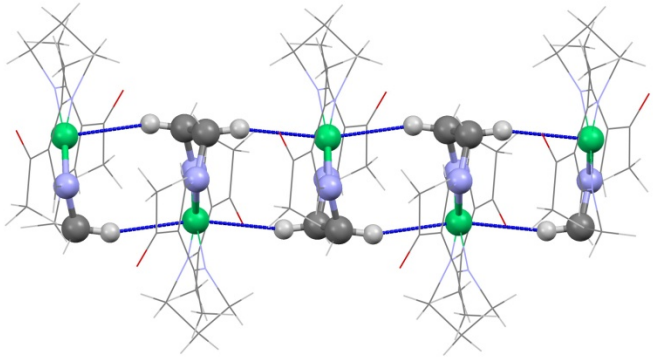


DOPXAI

(Acetato)-(2,4-di-t-butyl-6-((2-pyridinylmethyl)iminomethyl)phenolato)-nickel(II) methanol solvate

F. D. Lesh, S. S. Hindo, M. J. Heeg, M. M. Allard, P. Jain, B. Peng, L. Hryhorczuk and C. V. Verani, *Eur. J. Inorg. Chem*., 2009, 345.

d = 2.87 Å, θ = 140°; *d* = 2.90 Å, θ = 122°. Imine complex with ethylene bridge. Each methylene-H atom of a single methylene group forms an interaction leading to a linear supramolecular chain.

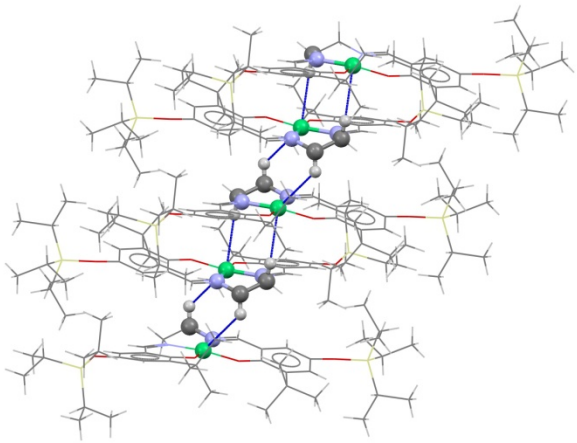


FEBSIO

(6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetra-azacyclopentadeca-4,6,12,14-tetraenato-N,N',N'',N''')-nickel(II) pyridine solvate

N. W. Alcock, W. K. Lin, A. Jircitano, J. D. Mokren, P. W. R. Corfield, G. Johnson, G., Novotnak, C. Caims and D. H. Busch, *Inorg. Chem*., 1987, **26**, 440.

d = 2.75 Å, θ = 157°; *d* = 2.84 Å, θ = 154°. Schiff base complex with ethylene bridge. Anti methylene-H atoms of the ethylene bridge forms an interaction leading to a linear supramolecular chain.

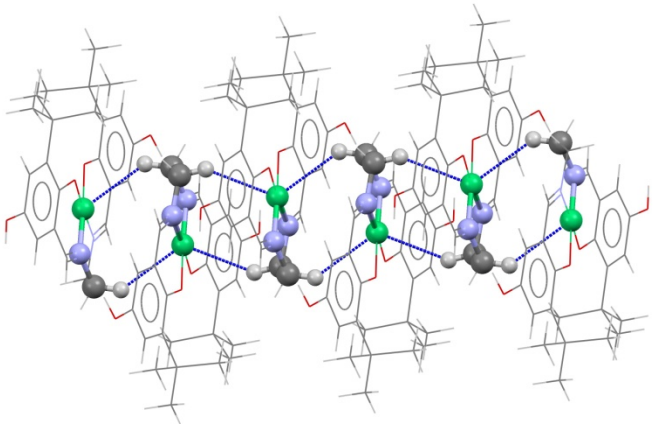


ICUHOE

(N,N'-bis(3-t-Butyl-2-oxy-5-(tri-isopropylsiloxy)benzylidene)ethylenediamine-N,N',O,O')-nickel(II)

G. Margraf, T. Kretz, F. F. De Biani, F. Laschi, S. Losi, P. Zanello, J. W. Bats, B. Wolf, K. Removic-Langer, M. Lang, A. Prokofiev, W. Assmus, H. W. Lerner and M. Wagner, *Inorg. Chem.*, 2006, **45**, 1277.

d = 2.88 Å, θ = 132° {two-fold symmetry}. Schiff base complex with ethylene bridge and two-fold symmetry. Anti methylene-H atoms of the ethylene bridge forms an interaction leading to a linear supramolecular chain.

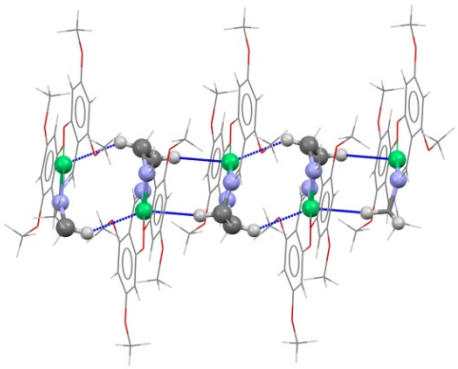


ICUJAS

(N,N'-bis(3-t-Butyl-5-hydroxy-2-oxybenzylidene)ethylenediamine-N,N',O,O')-nickel(IIi) methanol solvate

G. Margraf, T. Kretz, F. F. De Biani, F. Laschi, S. Losi, P. Zanello, J. W. Bats, B. Wolf, K. Removic-Langer, M. Lang, A. Prokofiev, W. Assmus, H. W. Lerner and M. Wagner, *Inorg. Chem.*, 2006, **45**, 1277.

d = 2.73 Å, θ = 137°; d = 2.80 Å, θ = 138°. Schiff base complex with ethylene bridge. Anti methylene-H atoms of the ethylene bridge forms an interaction leading to a linear supramolecular chain.

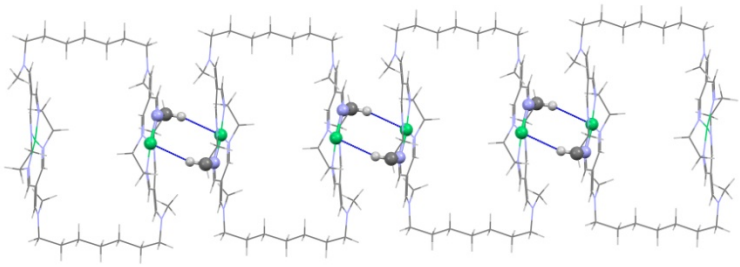


VUYCOI

(3,3',5,5'-Tetramethoxy-2,2'-(ethane-1,2-diylbis(nitrilomethylidyne))-diphenolato)-nickel(II)

G. E. Assey, R. J. Butcher and Y. Gultneh, *Acta Crystallogr. Sect. E: Struct. Rep. Online,* 2010, **66**, m620.

d = 2.73 Å, θ = 144°; d = 2.86 Å, θ = 144°. Schiff base complex with ethylene bridge. Anti methylene-H atoms of the ethylene bridge forms an interaction leading to a linear supramolecular chain.

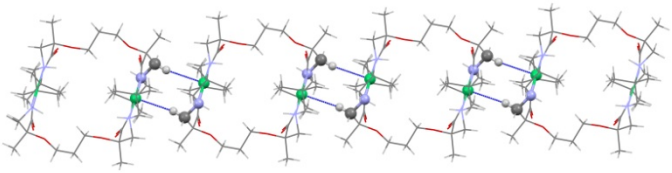


WEGLEA

(μ_2-3,11,15,18,22,30,34,37,40,43,46,49-Dodeca-aza-3,11,22,30-tetramethyltricyclo(30.6.6.6^{12,19})pentaconta-1,12,14,18,20,31,33,37,39,43,45,49-dodecaene)-di-nickel tetrakis(hexafluorophosphate) tetrahydrate

S. Domagała, A. Więckowska, J. Kowalski, A. Rogowska, J. Sydłowska, B. K. Daszkiewicz, R. Bilewicz and K. Woźniak, *Chem. Eur. J.*, 2006, **12**, 2967.

d = 2.86 Å, θ = 154° {centre of inversion}. Centrosymmetric oligomer encompassing two macrocycles with two imine groups. A methylene-H from each macrocycle forms an interaction leading to a linear supramolecular chain. Copper complex {WEGKID} associates in a similar fashion.

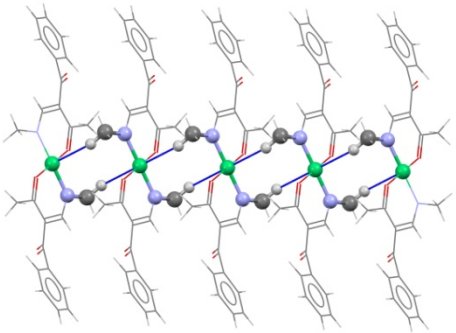


YUVBAS

(μ_2-6,6';13,13'-bis(Propanedioxy)-bis(3,3,6,10,10,13-hexamethyl-1,4,8,11-tetra-azacyclotetradecane-5,12-dione))-nickel(II) hemihydrate

S. Dumas, E. Lastra and L. S. Hegedus, *J. Am. Chem. Soc*., 1995, **117**, 3368.

d = 2.89 Å, θ = 149° {centre of inversion}. Two independent and centrosymmetric oligomers encompassing two macrocycles. A methylene-H, adjacent to the secondary amine, from one of the independent molecules, forms an interaction leading to a linear supramolecular chain.



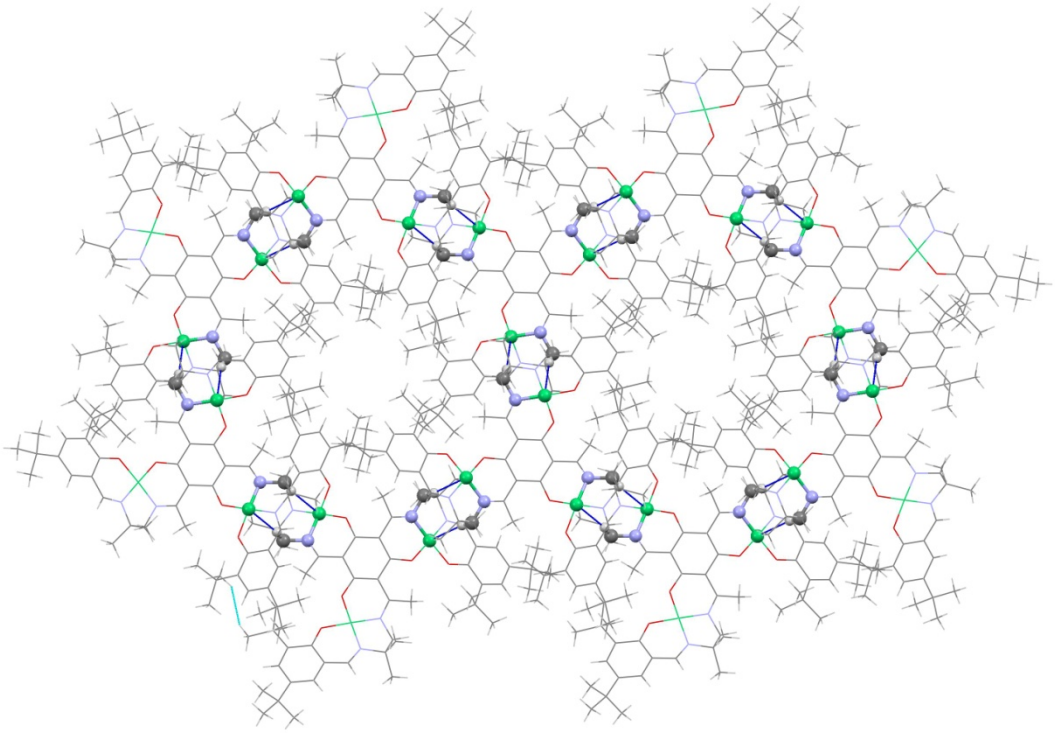
ZETQUK

bis(2-Acetyl-2-benzoyl-N-methylaminoethene)-nickel(II)

F. Wiesemann, B. Krebs, H. Gorls and E. G. Jager, *Z. Anorg. Allg. Chem*., 1995, **621**, 1883.

d = 2.56 Å, θ = 165° {centre of inversion}. Centrosymmetric complex where the methyl-H from a coordinated azanide-N forms the interaction leading to a linear supramolecular chain.

TWO-DIMENSIONAL ARRAY



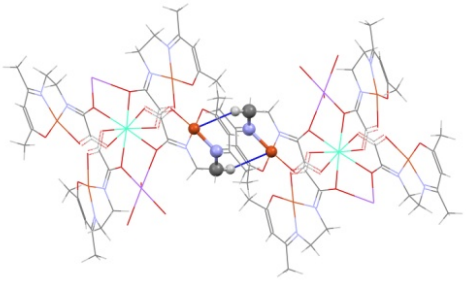
WAQVEQ

(μ_3-2,4,6-tris(1-(2-(3,5-Di-t-butylsalicylideneamino)-2-methylpropylimino)ethyl)-benzene-1,3,5-triolato)-tri-nickel(II)

T. Glaser, M. Heidemeier, R. Frohlich, P. Hildebrandt, E. Bothe and E. Bill, *Inorg. Chem.*, 2005, **44**, 5467.

d = 2.72 Å, θ = 165° {three-fold symmetry}. Trinuclear complex with three Schiff base residues, with (dimethyl)ethylene bridges, cleaved onto a central benzene ring – three-fold symmetry. One methylene-H from each forms an interaction to generate a two-dimensional array. The copper complex {**HIWSAI**} forms a similar arrangement.

Table S(3). Diagrams and details of self-assembled zero-dimensional aggregates mediated by {...HCNCu}$_2$ synthons in molecular copper complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

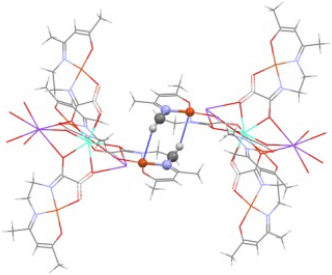


ALATIR

catena-[tetrakis(μ$_3$-N-(4-Methyl-6-oxy-3-azahepta-3,5-dienyl)oxamato)-aqua-tetra-copper(II)-gadolinium(III)-sodium methanol solvate]

Y. Maruno, K. Yabe, T. Fujinami, N. Matsumoto, N. Re and J. Mrozinski, *Bull. Chem. Soc. Jpn*. 2010, **83**, 1511.

d = 2.98 Å, θ = 160° {centre of inversion}. Ionic (Cu neutral) and heterometallic (Gd) complex featuring four pendent Schiff base complexes with ethylene bridges. The ions associate to form a linear chain. These are connected into a two-dimensional array by interactions involving methylene-H atoms.

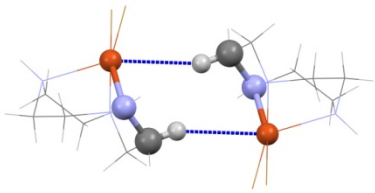


ALATOX

catena-[bis(μ$_4$-N-(4-Methyl-6-oxy-3-azahepta-3,5-dienyl)oxamato)-bis(μ$_3$-N-(4-methyl-6-oxy-3-azahepta-3,5-dienyl)oxamato)-aqua-tetra-copper(II)-gadolinium(III)-potassium methanol solvate]

Y. Maruno, K. Yabe, T. Fujinami, N. Matsumoto, N. Re and J. Mrozinski, *Bull. Chem. Soc. Jpn*., 2010, **83**, 1511.

d = 2.79 Å, θ = 162° {centre of inversion}. Ionic (Cu neutral) and heterometallic (Gd) complex featuring four pendent Schiff base complexes with ethylene bridges. The ions associate to form a linear chain. These are connected into a two-dimensional array by interactions involving methylene-H atoms.

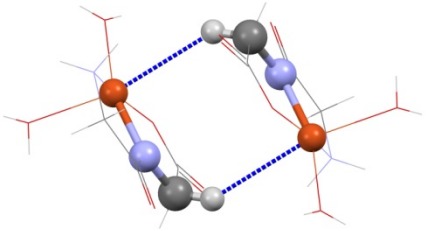


BAZNCU

Dibromo-(1,4,7-triazacyclononane)-copper(II)

R. D. Bereman, M. R. Churchill, P. M. Schaber and M. E. Winkler, *Inorg. Chem*., 1979, **18**, 3122.

d = 2.84 Å, θ = 159° {centre of inversion}. Macrocycle with ethylenediamine-type links. Molecules associate via methylene-H atoms.



CGLGLT01, CGLGLT02, CGLGLT03 & CGLGLT04

Diaqua-(glycylglycinato)-copper(II) monohydrate

I. Bytheway, B. N. Figgis and A. N. Sobolev, *J. Chem. Soc. Dalton Trans*., 2001, 3285.

Two independent molecules

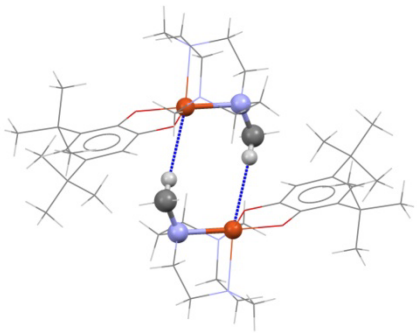
d = 2.83 Å, θ = 138° {centre of inversion} – room temperature

d = 2.83 Å, θ = 133°; d = 2.97 Å, θ = 135° {centre of inversion} – 10 K

d = 2.68 Å, θ = 135°; d = 2.83 Å, θ = 136° {centre of inversion} – 10 K

d = 2.85 Å, θ = 131°; d = 2.96 Å, θ = 135° {centre of inversion} – 10 K

Different refinement strategies. Two independent molecules and each associates *via* methylene-H atoms adjacent to the azanide-N atom.



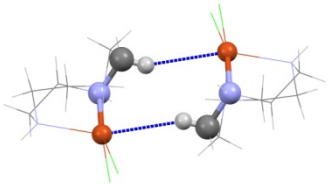
CINDEI

(3,5-Di-t-butyl-1,2-catecholato)-(1,4,7-trimethyl-1,4,7-triazacyclononane)-copper tetrahydrofuran solvate

J. Rall, M. Wagner, M. Albrecht, F. Homung, W. Kaim, Chem. Eur, J. 1999, 5, 2802.

Two independent molecules

d = 2.77 Å, θ = 154° {centre of inversion}; d = 2.71 Å, θ = 151° {centre of inversion}. Macrocycle with ethylenediamine-type links. Two independent molecules and each associates *via* N-methyl-H atoms.

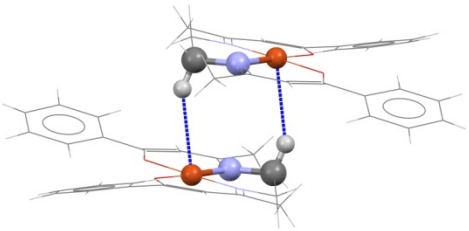


CLAZCU

Dichloro-(1,4,7-triazacyclononane)-copper(II)

W. F. Schwindinger, T. G. Fawcett, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *Inorg. Chem*., 1980, **19**, 1379.

d = 2.86 Å, θ = 157° {centre of inversion}. Macrocycle with ethylenediamine-type links. Molecules associate *via* methylene-H atoms.



COSXOX, COSXOX01 & COSXOX02

(1,1'-Diphenyl-3,3'-(ethylenedi-imino)-di-1-butanonato)-copper(II)

K. M. A. Malik, S. Z. Halder, A. Hashem and M.B.Hursthouse, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 29.

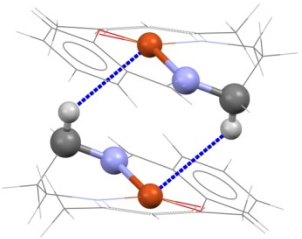
d = 2.65 Å, θ = 152° {centre of inversion}.

Y. Eleman, H. Kara and H. Fuess, *Private Communication to the CSD*, 1999.

d = 2.82 Å, θ = 148° {centre of inversion}.

S. Dehghanpour, F. Mojahed and F. Farzaneh, *Z. Kristallogr., New Cryst. Struct.*, 2005, **220**, 587.

d = 2.80 Å, θ = 146° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate via methylene-H.

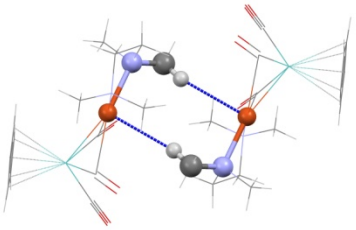


DAZMAS

(Trimethylene-N-(acetylacetoneiminato)-N'-salicylideneiminato-N,N',O,O')-copper(II)

N. Matsumoto, M. Asakawa, H. Nogami, M.Higuchi and A. Ohyoshi, *J. Chem. Soc. Dalton Trans.*, 1985, 101.

d = 2.92 Å, θ = 122° {centre of inversion}. Schiff base with propylene bridge. Molecules associate via α-methylene-H.

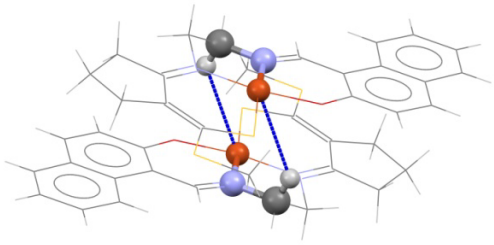


DEZYOW

bis(μ_2-Carbonyl)-(carbonyl-(η^5-cyclopentadienyl)-molybdenum)-(N,N,N',N'-dimethylethylenediamine-N,N')-copper

G. Doyle, K. A. Eriksen and D. Van Engen, *Organometallics*, 1985, **4**, 2201.

d = 2.89 Å, θ = 138° {centre of inversion}. Tetramethylethylenediamine ligand. Molecules associate via N-methyl-H.

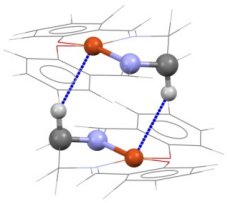


DIRZIO

(1-(((2-((2-((Methylsulfanyl)(sulfanyl-S)methylene)cyclopentylidene)-amino-N)ethyl)imino-N)methyl)-2-naphtholato-O)-copper(II)

E. Pereira, L. R. Gomes, J. N. Low and B. De Castro, *Polyhedron*, 2008, **27**, 335.

d = 2.93 Å, θ = 132° {centre of inversion}. Schiff base with ethylene bridge. Two independent molecules but only one self-associates, *via* a methylene-H.

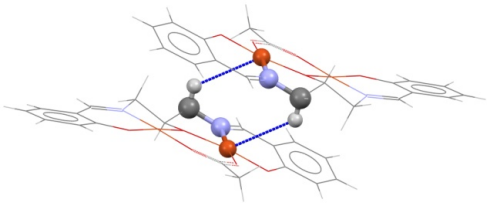


ESALCT

N,N'-Ethylenebis(salicylaldiminato) copper(II) thiourea

M. B. Ferrari, G. G. Fava and C. Pelizzi, *Acta Crystallogr. Sect. B: Struct. Crystallogr. Struct. Chem.*, 1976, **32**, 901.

d = 2.77 Å, θ = 131° {centre of inversion}. Schiff base with ethylene bridge. Molecules associate *via* a methylene-H interactions.

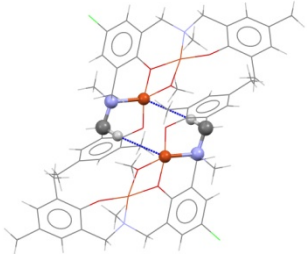


FAPGOS01

(μ_2-Acetato)-(μ_2-1,3-bis(salicylaldiminato)propan-2-olato)-di-copper(II) methanol solvate

V. V. Lukov, V. A. Kogan, Yu. P. Tupolova, L. D. Popov, I. E. Gevorkyan, V. V. Tkachev, G. V. Shilov and D. D. Makotova, *Zh. Neorg, Khim.*, 2004, **49**, 1993.

d = 2.97 Å, θ = 129° {centre of inversion}. Two imine groups bridged by a propylene bridge with central oxide. Molecules associate via N-methylene-H.

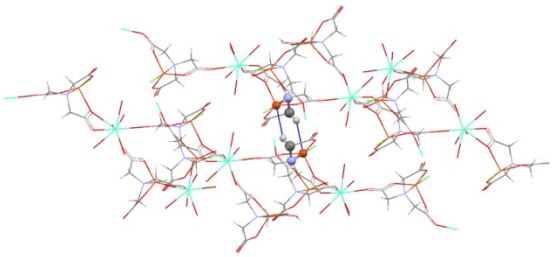


FEFQEM

(μ_2-Methoxo)-(μ_2-2,6-bis(N-(3,5-dimethyl-2-oxobenzyl)-N-methylaminomethyl)-4-chlorophenoxo)-di-copper(II) methanol solvate

P. Amudha, M. Kandaswamy, I. Govindasamy and D. Velmurugan, *Inorg. Chem.*, 1998, **37**, 4486.

d = 2.92 Å, θ = 143° {centre of inversion}. Tetradentate N_2O_2 ligand linking two Cu atoms. Molecules associate *via* methylene-H.

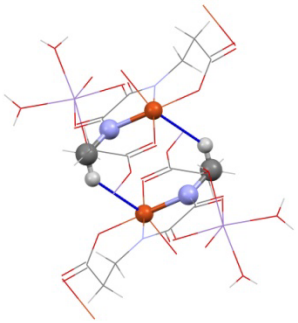


FIDLEK

catena-[Tetra-sodium octakis(μ3-nitrilotriacetato)-hexadeca-aqua-octachloro-octa-copper(II)-tetra-gadolinium(III)]

H. Z. Kou, Y. B. Jiang and A. L. Cui, *Cryst. Growth Des*., 2005, **5**, 77.

d = 2.95 Å, θ = 152° {centre of inversion}. Ionic (neutral Cu) and heterometallic (Gd and Na) complex with eight pendent Cu[(tricarboxyale)amine] ligands, one of which self-associates via methylene-H (linking N to CO_2).

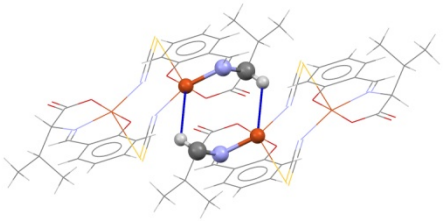


FURRUF

catena-[(μ4-Oxamido-bis(propionato)-N,N',O,O',O'',O''')-triaqua-copper(II)-manganese(II) monohydrate]

Y. Pei, O. Kahn, J. Sletten, J. P. Renard, R. Geprges, J. C. Glanduzzo, J. Curely and Q. Xu, *Inorg. Chem*., 1998, **27**, 47.

d = 2.78 Å, θ = 137° {centre of inversion}. Molecules are linked into a chain. Chains are linked into a two-dimensional array by methylene-H interactions.

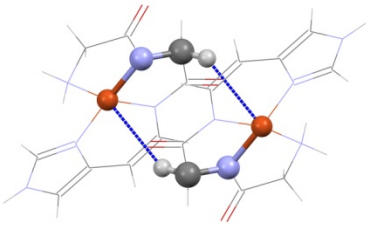


GADNAB

Di-potassium bis[(μ2-isothiocyanato-N,S)-(N-salicylidene-DL-valinato-N,O,O')-copper(II)]

J. Vanco, O. Svajlenova and J. Marek, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun*., 2003, **59**, m190.

d = 2.96 Å, θ = 126° {centre of inversion}. Complex with imine group. Molecules associate via methine-H.

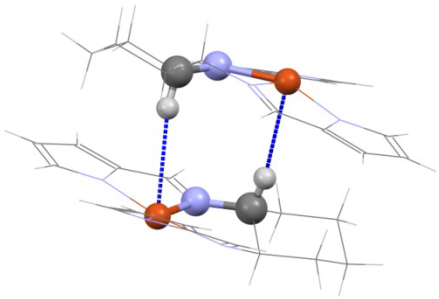


GGDHCU10

a,b-Didehydro-glycylglycyl-histaminato-copper(II) dihydrate

P. De Meester and D. J. Hodgson, *Inorg. Chem.*, 1978, **17**, 440.

d = 2.91 Å, θ = 140° {centre of inversion}. Peptide with molecules connected via methylene-H (between N and C=O).

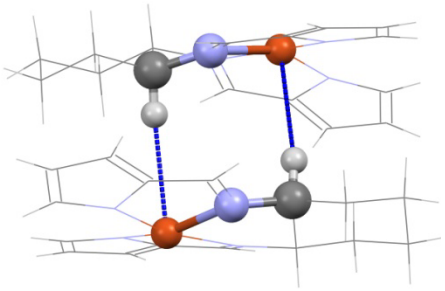


GICPAK

((1R,2R)-N1,N2-bis((Pyrrol-2-yl)methylene)cyclohexane-1,2-diamine)-copper(II)

Y. Wang, H. Fu, F. Shen, X. Sheng, A. Peng, Z. Gu, H. Ma, J. S. Ma and J. Yao, *Inorg. Chem.*, 2007, **46**, 3548.

d = 2.69 Å, θ = 164°; d = 2.84 Å, θ = 171°. Schiff base with cyclohexyl bridge. Two independent molecules associate *via* methine-H.

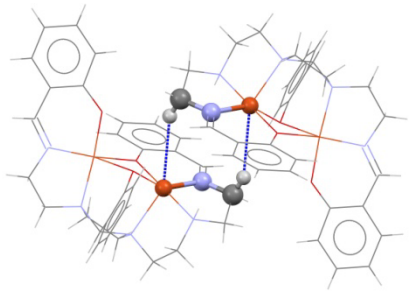


GIHJUD

((1S,2S)-N1,N2-bis((Pyrrol-2-yl)methylene)cyclohexane-1,2-diamine)-copper(II)

Y. Wang, H. Fu, F. Shen, X. Sheng, A. Peng, Z. Gu, H. Ma, J. S. Ma and J. Yao, *Inorg. Chem.*, 2007, **46**, 3548.

d = 2.70 Å, θ = 165°; d = 2.83 Å, θ = 171°. Schiff base with cyclohexyl bridge. Two independent molecules associate *via* methine-H.

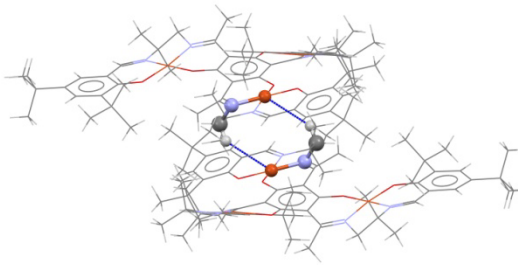


HETWIN

(μ_2-2-(2-Oxyphenyl)-1-(2-(2-oxybenzyl)aminoethyl)-3-(2-(2-oxybenzyl)-bis(aminoethyl))imidazolidine)-di-copper(II) nitrate trihydrate

Q. Y. Du, J. G. Wang, J. H. Qin and F. Y. Ju, *Z. Kristallogr. - New Cryst. Struct.* 2006, **221**, 489.

d = 2.90 Å, θ = 136° {centre of inversion}. Hexdentate N_5O ligand encompassing two Cu centres. Molecules associate via imine-methylene-H.

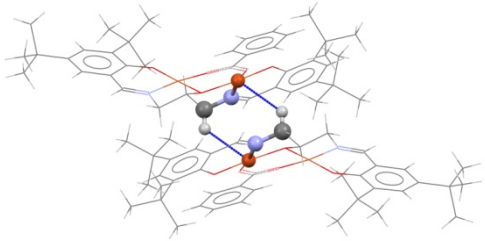


HIWRUB

(μ_3-2,4,6-tris(1-(2-(3,5-Di-t-butylsalicylidene-amino)-2-methylpropylimino)ethyl)-benzene-1,3,5-triolato)-tri-copper(II) n-heptane dichloromethane solvate

T. Glaser, M. Heidemeier, J. B. H. Strautmann, H. Bogge, A. Stammier, E. Krickemeyer, R. Huenerbein, S. Grimme, E. Bothe and E. Bill, *Chem. Eur. J.*, 2007, **13**, 9191.

d = 3.00 Å, θ = 144° {centre of inversion}. Trinuclear complex with three Schiff bases with (di-methyl)ethylene bridges. One of these associates *via* methylene-H.

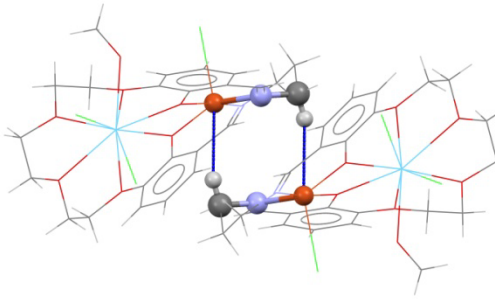


HOWYUO

(μ_2-Benzoato-O,O')-(μ_2-1,3-bis(3,5-di-t-butylsalicylideneamino)-propan-2-olato-N,N',O,O',O'')-di-copper(II) dimethyl-formamide solvate

Y. Kou, J. Tian, D. Li, W. Gu, X. Liu, S. Yan, D. Liao and P. Cheng, *Dalton Trans.*, 2009, 2374.

d = 2.75 Å, θ = 129° {centre of inversion}. Two independent binuclear molecules comprise the asymmetric unit. One of these associates via imine-methylene-H.

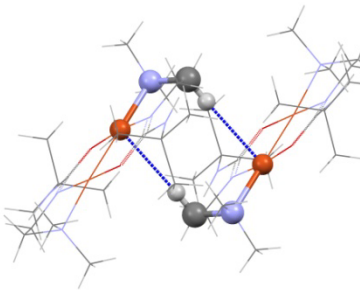


ICAFOI

(μ_2-N,N'-(3,3'-(3,6-dioxaoctane-1,8-dioxy)bis(salicylidenato))-1,3-diamino-propane)-trichloro-methanol-lanthanum(III)-copper(II)

A. Caneschi, L. Sorace, U. Casellato, P. Tomasin and P. A. Vigato, *Eur. J. Inorg. Chem.*, 2004, 3887.

d = 2.98 Å, θ = 131° {centre of inversion}. Heterometallic complex (La) where Schiff base residue (propylene bridge) is connected to La. Molecules associate *via* α-methylene-H.

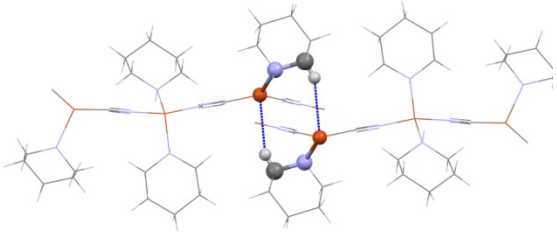


IWEHEX

bis(μ_2-N'-t-butylaminocarbonyl-2-(N,N-dimethylamino)ethylamido)-di-copper(I) tetrafluoroborate

R. Gupta, Z. H. Zhang, D. Powell, M. P. Hendrich and A. S. Borovik, *Inorg. Chem.*, 2002, **41**, 5100.

d = 2.79 Å, θ = 169° {centre of inversion}. Ionic binuclear complex (Cu cation) with three independent species (two are centrosymmetric). One self-associates via tertiary-amine-methylene-H.

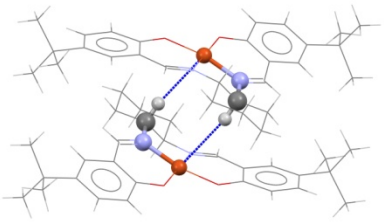


JEYFAV

catena-(tris(μ_2-cyano)-tetrakis(piperidine-N)-tri-copper(I))

G. A. Bowmaker, C. Pettinari, B. W. Skelton, N. Spmers, N. A. Vigar and A. H. White, *Z. Anorg. Allg. Chem.*, 2007, **633**, 415.

d = 2.87 Å, θ = 155° {centre of inversion}. This is a coordination polymer by virtue of μ-CN bridging. As Cu...H–C–N hydrogen bonding (piperidine-methylene-H) only connects pairs, the motif is considered zero-dimensional.

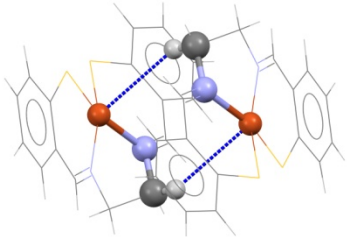


KAVWIO

(N,N'-bis(2-hydroxy-5-t-butylbenzylidene)-trans-1,2-dicyclohexylamine)copper(II) dichloromethane solvate

I. Skylvestre, J. Wolowska, C. A. Kilner, E. J. L. Mclnnes and M. A. Halcrow, *Dalton Trans*., 2005, 3241.

d = 2.93 Å, θ = 167° {centre of inversion}. Schiff base with cyclohexyl bridge. Molecules associate *via* methane-H.

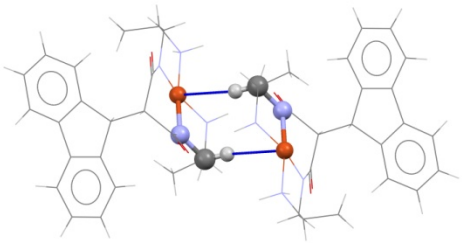


MELJAO

(N,N'-Ethylene-bis(thiosalicylidene)imine)-copper(II)

N. Goswami and D. M. Eichhorn, *Inorg. Chim. Acta*, 2000, **303**, 271.

d = 2.96 Å, θ = 129° {centre of inversion}. Schiff base complex with ethylene bridge. Two independent molecules and one self-associates *via* methylene-H.

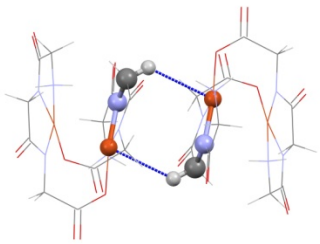


MIMLAV

(2,10-Diamino-6-(9H-fluoren-9-yl)-4,8-diazaundecane-4,8-diyl-5,7-dione-N,N',N'',N''')-copper(II) dihydrate

L. J. Jiang, Q. H. Luo, Q. X. Li, M. C. Shen and H. W. Hu, *Eur. J. Inorg. Chem*., 2002, 664.

d = 2.99 Å, θ = 157° {centre of inversion}. Complex with two imine groups. Molecules associate via imine-methylene-H.

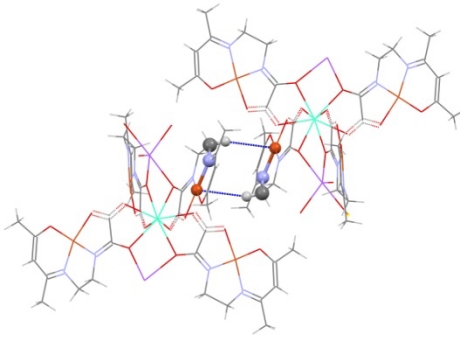


NGGGCU01

Di-sodium bis(μ_2-glycylglycylglycinato)-di-copper dihydrate

H. C. Freeman, J. C. Schoone, J. G. Sime, *Acta Crystallogr*., 1965, **18**, 381.

d = 2.87 Å, θ = 128° {centre of inversion}. Ionic complex (Cu anion). Molecules associate into a two-dimensional array. Interactions of the type methylene-H, from a –N-CH_2–C(=O)–, connect centrosymmetrically related pairs into a three-dimensional architecture.

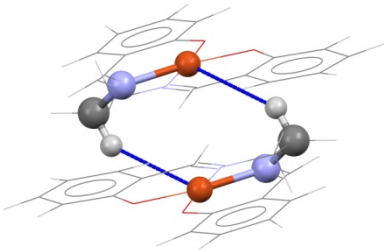


NIVNIQ

catena-(tetrakis(μ_3-N-(4-Methyl-6-oxy-3-azahepta-3,5-dienyl)oxamato)-aqua-tetra-copper(II)-gadolinium(III)-sodium methanol solvate dihydrate)

K. Yabe, Y. Maruno, M. Towatari, T. Hamamatsu, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *Chem. Lett.*, 2007, **36**, 1452.

d = 2.97 Å, θ = 159° {centre of inversion}. Ionic (neutral Cu) and heteronuclear (Gd) complex where there are four Schiff base residues, ethylene bridge. One of these self-associates *via* methylene-H.

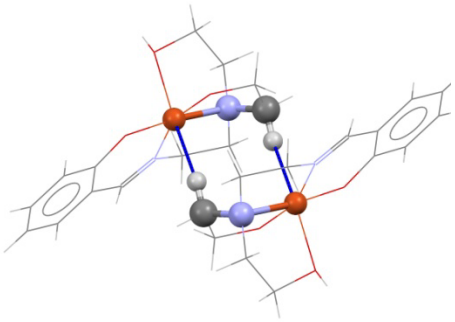


NPOSAC

p-Nitrophenol-N,N'-ethylene bis(salicylideneiminato) copper(II)

E. N. Baker, D. Hall and T. N. Waters, *J. Chem. Soc. A*, 1970, 400.

d = 2.96 Å, θ = 143° {centre of inversion}. Schiff base complex, ethylene bridge. Molecules associate via methylene-H.

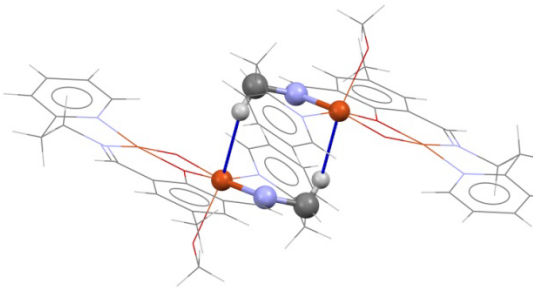


ODALAG

(N-Salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine)-copper(II) (N-salicylidene-2-(2-hydroxyethyl(2-oxyethyl)amino)ethylamine)-copper(II) tetrafluoroborate monohydrate

W. Plass, A. Pohlmann and J. Rautengarten, *Angew. Chem. Int. Ed.*, 2001, **40**, 4207.

d = 2.78 Å, θ = 148° {centre of inversion}. Ionic complex with neutral and formally cationic Cu centres. The neutral species self-associates via tertiary-amine-methylene-H. While the cationic Cu centre might be anticipated to form a charge-assisted interaction, the proximate hydroxyl groups form hydrogen bonds effectiviely shielding the Cu atom from further interactions.

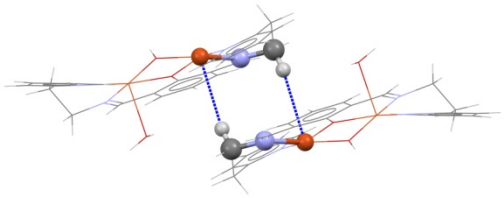


PEVCAV

(μ_2-Hydroxo)-(μ_2-2,6-bis(N-(2-pyridylethyl)formidoyl)-4-methylphenolato)-(methanol)-di-copper(II) bis(methyl 3,4-dioxybenzoate)-copper(II) perchlorate

J. Manzur, A. M. Garcia, A. Vega and A. Ibanez, *Polyhedron*, 2007, **26**, 115.

d = 2.91 Å, θ = 135° {centre of inversion}. The asymmetric unit comprises a neutral mononuclear complex, a cationic binuclear complex with the charge balance provided by a perchlorate. One of the Cu atoms of the binuclear complex forms an imine-methylene-H interaction.

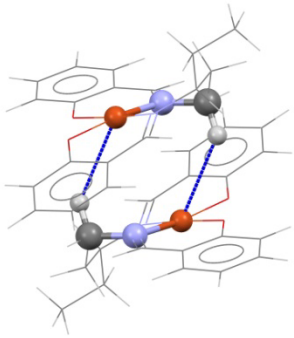


POYNOG

*(μ_2-Hydroxo)-[μ_2-2,6-bis(N-(2-(2-pyridyl)ethyl)formimidoyl) phenolato)-aqua-di-copper(**I**) bis(tetrafluoroborate]*

S. Ryan, H. Adams, D. E. Fenton, M. Becker and S. Schindler, *Inorg. Chem.*, 1998, **37**, 2134.

d = 2.96 Å, θ = 156° {centre of inversion}. Ionic binuclear complex (cation shared over both centres) with four- and five-coordinate Cu centres and with Cu coordinated by a Schiff base reside (ethylene bridge). The four-coordinate Cu centres associate via methylene-H.

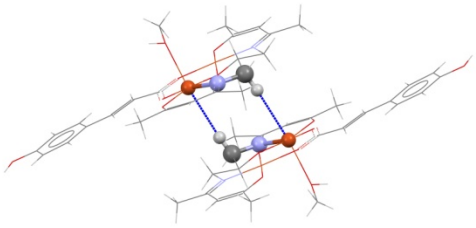


PUVHUJ

1,3-bis(2-Hydroxybenzylideneamino)pentane-copper(II) ethanol solvate

T. H. Lu, H. H. Yao, J. M. Lo and S. F. Tung, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 1600.

d = 2.95 Å, θ = 129° {centre of inversion}. Two independent Schiff base molecules with (ethyl)ethylene bridge. One self-associates via methylene-H.

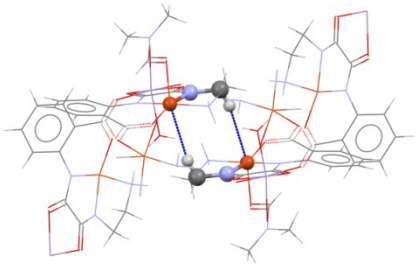


QAXCUO

(μ_2-1,3-bis(Acetylacetoneimine)propan-2-ol)-(μ_2-p-hydroxycinnamato)-(methanol)-di-copper(II) methanol solvate

S. Gupta, A. Mukherjee, M. Nethaji and A. R. Chakravarty, *Polyhedron*, 2005, **24**, 1922.

d = 2.79 Å, θ = 175° {centre of inversion}. Binuclear complex with N_4O pentadentate ligand. One Cu associates via imine-methylene-H.

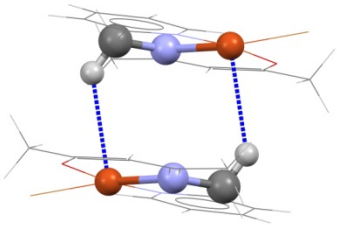


TUSWOT

catena-[bis(μ_3-N-Benzoato-N'-(2-aminoethyl)-oxamido)-aqua-(dimethyl-formamide)-di-copper(II)-manganese(II) dimethylformamide solvate monohydrate]

S. Q. Zang, R. J. Tao, Q. L. Wang, N. H. Hu, Y. X. Cheng, J. Y. Niu and D. Z. Lia, *Inorg. Chem*., 2003, **42**, 761.

d = 2.93 Å, θ = 165° {centre of inversion}. Heteronuclear (Mn) Schiff base complex with propylene bridge. Molecules self-associate via α-methylene interactions.

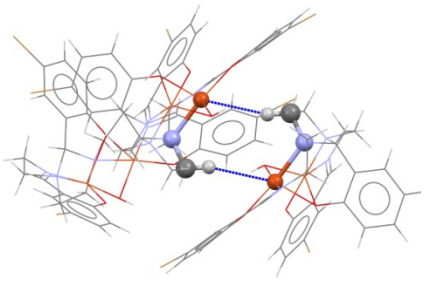


VATZIA

(N-(1-acetyl-2-propylidene)(2-pyridylmethyl)amine-N,N',O)-bromine-copper(II)

R. Kamakar, C. R. Choudhary, A. S. Batsanov, S. R. Batten and S. Mitra, *Struct. Chem*., 2005, **16**, 535.

d = 2.73 Å, θ = 135° {centre of inversion}. Tridentate N_2O ligand with imine group. Molecules associate via methylene-H.

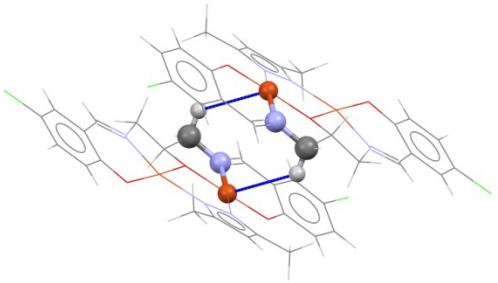


XAXWEZ

(μ$_2$-Aqua)-(μ$_2$-1,3-bis(2-((5-bromo-2-oxypheny)lmethyleneamino)ethyl)-2-(5-bromo-2-oxyphenyl)imidazolidine)-di-copper(II) acetonitrile solvate hydrate

M. Fondo, N. Ocampo, A. M. Garcia-Deibe, M. Corbella, M. R. Bermejo and J. Sanmartin, *Dalton Trans*., 2005, 3785.

d = 2.92 Å, θ = 163° {centre of inversion}. Two independent binuclear molecules (featuring –NCH$_2$CH$_2$N– residues) in the asymmetric unit. Molecules associate *via* methylene-H.

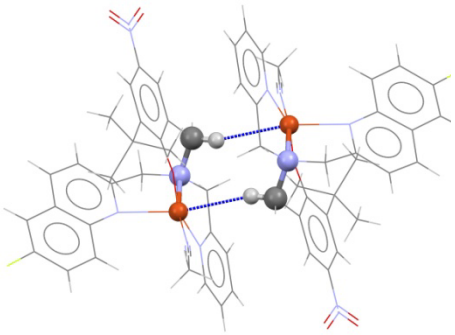


XEFSAC

(μ$_2$-1,3-bis(5-Chlorosalicylaldiminato)propan-2-olato)-(μ$_2$-3,5-dimethylpyrazolato)-di-copper(II)

H. Kara, Y. Elerman and K. Prout, *Z. Naturforsch., B: Chem. Sci*., 2000, **55**, 796.

d = 2.96 Å, θ = 127° {centre of inversion}. Binuclear complex with pentadentate N$_4$O ligand and imine groups. Molecules self-associate *via* methylene-H. Molecules also associate *via* Cu….O to lead to a linear supramolecular chain.

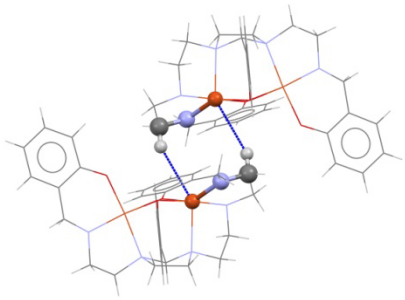


XERJOU

(acetonitrile-N)-(2-t-butyl-6-(((6-fluoroquinolin-2-ylmethyl)(pyridin-2-ylmethyl)amino)methyl)-4-nitrophenolato-N,N',N'',O)-copper(II) perchlorate

F. Michel, S. Hamman, F. Thomas, C. Philouze, I. Gautier-Luneau and J. L. Piere, *Chem. Commun*., 2006, 4122.

d = 2.69 Å, θ = 151° {centre of inversion}. Molecule has a tertiary amine and one of the methylene-H forms the interaction.

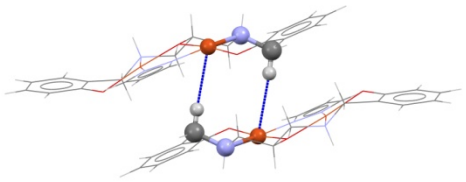


XOMZOO

(μ_2-2-(2-Hydroxyphenyl)-1-(2-(2-hydroxy-benzyl)aminoethyl)-3-(2-(2-(2-hydroxy-benzyl)aminoethyl)aminoethyl)-1,3-diazolidine)-di-copper(II) perchlorate acetonitrile solvate dihydrate

T. B. Lu, Y. W. Li, X. L. Feng, J. W. Cai, X. Y. Li and L. N. Ji, *Chem. Res. Chin. Univ.*, 2001, **17**, 148.

d = 2.93 Å, θ = 137° {centre of inversion}. Cationic binuclear molecule features –NCH_2CH_2N– residues and associate *via* methylene-H.

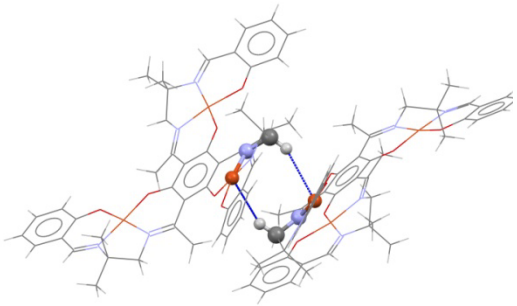


XUJRUP

(μ_2-Pyrazolato)-(μ_2-1,3-bis(2-hydroxybenzylamino)-2-propanolato)-di-copper(II)

S. C. Courtney, K. S. Murray and E. R. T. Tiekink, *Z. Kristallogr., New Cryst. Struct.*, 2002, **217**, 217.

d = 2.78 Å, θ = 163° {centre of inversion}. Binuclear molecule with pentadentate N_2O_3 ligand with methylene bridges. Molecules associate *via* methylene-H.

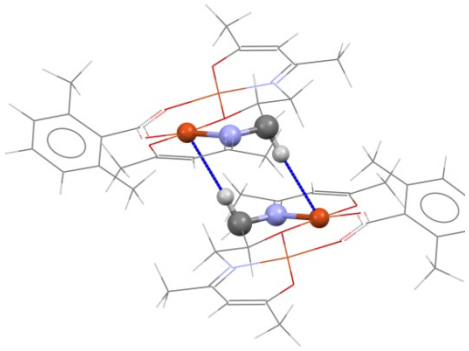


YADNOH

(μ_3-2,4,6-tris(1-(2-Salicylaldimino-2-methyl-propylimino)ethyl)-1,3,5-trihydroxy-benzene)-tri-copper(II) chloroform toluene solvate

T. Glaser, M. Heidemeier, S. Grimme and E. Bill, *Inorg. Chem.*, 2004, **43**, 5192.

d = 2.94 Å, θ = 151° {two-fold symmetry}. Trinuclear molecule with three Schiff base residues and (ethyl)methylene bridges. One self-associates via methylene-H.

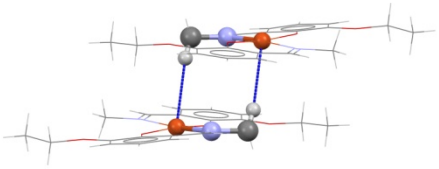


YAKDUJ

(μ_2-2,6-Dimethylbenzoato)-(μ_2-4,10-dimethyl-5,9-diaza-2,4,9,11-tridecatetraene-2,7,12-triolato)-di-copper(II)

T. Kawata, M. Yamanaka, S. Obha, Y. Nishida, M. Nagamatsu, T. Tokii, M. Kato and O. W. Steward, *Bull. Chem. Soc. Jpn*., 1992, **65**, 2739.

d = 2.76 Å, θ = 173° {centre of inversion}. Binuclear molecule with pentadentate N_4O ligand and imine groups. One Cu centre associates *via* imine-methylene-H.



ZEMLOS

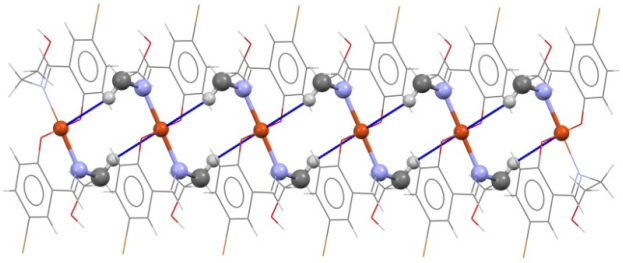
bis(N-Methyl-3-ethoxysalicyclideneaminato)-copper(II)

B. Kamenar, A. Stefanovic and I. Zigrovic, *Z. Kristallogr*., 1995, **210**, 662.

d = 2.91 Å, θ = 169° {centre of inversion}. Complex feature an imine group and associates *via* imine-methyl-H.

Table S(4). Diagrams and details of self-assembled supramolecular 1-D chains and 2-D layers mediated by {...HCNCu}$_2$ synthons in molecular copper complexes. Aggregates are arranged in order of their CSD REFCODES. Only interacting species from each structure are illustrated, *e.g.* solvent molecules, counter ions, *etc*. are omitted.

ONE-DIMENSIONAL CHAINS



HEDKUX, HEDKUX01

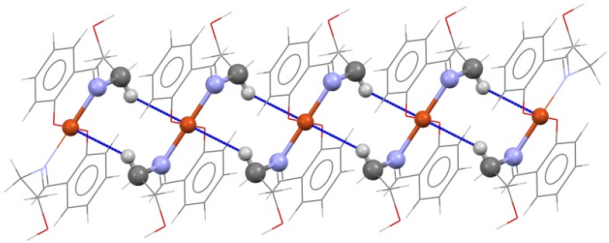
bis(N-(5-Bromosalicylidene)-2-aminoethanol-N,O')-copper(II)

F. Z. Liang, J. P. Ma and J. H. Zhu, *Chin. J. Inorg. Chem*., 2006, **22**, 115.

d = 2.81 Å, θ = 138° {centre of inversion}.

Y. M. Chumakov, V. I. Tspkov, G. Bocelli, B. Y. Antosyak and P. Gulya, *Kristallografiya*, 2007, **52**, 227.

d = 2.82 Å, θ = 139° {centre of inversion}. The centrosymmetric complex has imine groups and associates into a linear supramolecular chain via imine-methylene-H interactions.



HESLCU02, HESLCU04 & HESLCU07

bis(N-2-Hydroxyethylsalicylaldiminato)-copper(II)

F. Nepveu and H. Paulus, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun*., 1985, **41**, 858.

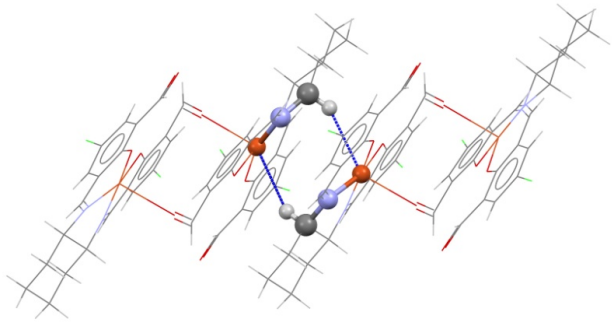
d = 2.83 Å, θ = 124° {centre of inversion}.

B. Kamenar, A. Stefanovic and B. Sorgic, *Z. Kristallogr*. 1995, 210, 728.

d = 2.80 Å, θ = 124° {centre of inversion}.

A. C. D. Midoes, P. E. Aranha, M. P. Dos Santos, E. Tozzo, S. Romera, R. H. de Santos and E. R. Dockal, *Polyhedron*, 2008, **27**, 59.

d = 2.82 Å, θ = 123° {centre of inversion}. Two independent centrosymmetric complexes comprise the asymmetric unit, each having imine groups. One molecule self-associates into a linear supramolecular chain *via* imine-methylene-H. n.b. Other structures with CSD codes HESLCU0X do not have fractional atomic coordinates for the hydrogen atoms.

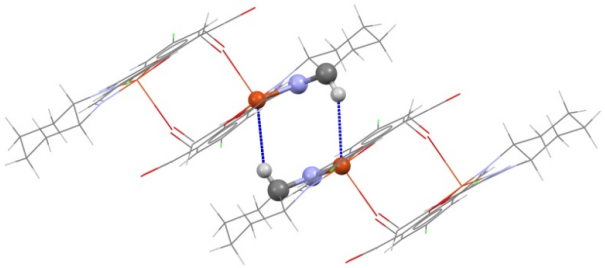


LOCTIH

(R,R)-bis(μ$_2$-1,2-bis((5-Chloro-3-formyl-2-oxybenzylidene)amino)cyclohexane)-di-copper(II)

W. Huang, Z. Chu and J. Jiang, *Polyhedron*, **27**, 2705.

d = 2.77 Å, θ = 147°; *d* = 2.82 Å, θ = 151°. Binuclear Schiff base complex with cyclohexyl bridge. Molecules associated into a linear supramolecular chain via methine-H interactions.

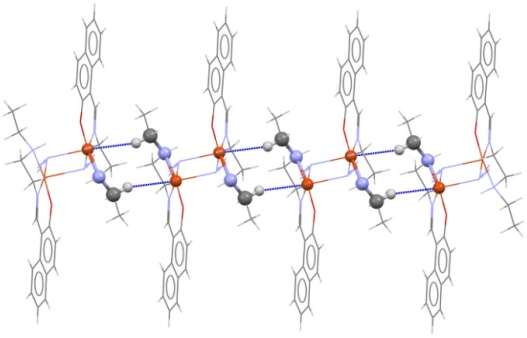


NOGZIT

(S,S)-bis(μ$_2$-1,2-bis((5-Chloro-3-formyl-2-oxybenzylidene)amino)cyclohexane)-di-copper(II)

W. Huang, Z. Chu and J. Jiang, *Polyhedron*, 2008, **27**, 2705.

d = 2.78 Å, θ = 147°; *d* = 2.86 Å, θ = 151°. Binuclear Schiff base complex with cyclohexyl bridge. Molecules associate into a linear supramolecular chain via methine-H interactions.

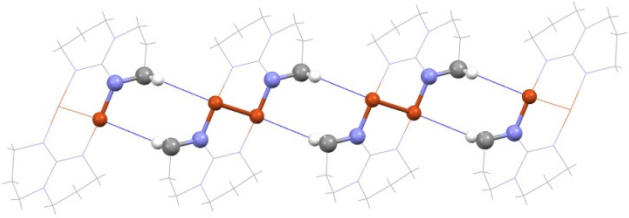


NUGLAD

bis(μ_2-Azido-N,N)-(bis(1-(((2-(ethylamino)ethyl)imino)methyl)-2-naphtholato))-di-copper(II)

R. H. Hui, P. Zhou and Z. L. You, *Indian J. Chem. Sect. A*, 2009, **48**, 1102.

d = 2.82 Å, θ = 157° {centre of inversion}. Binuclear and centrosymmetric Schiff base complex with ethylene bridge. Molecules associate into a linear supramolecular chain *via* N-methylene-H interactions (from a terminal N-ethyl group).

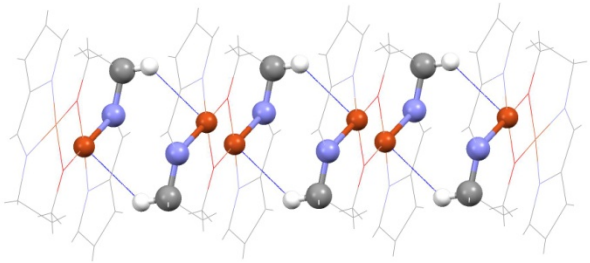


PIMXAK

*Bis[(μ_2-1,3,4,6,7,8-Hexahydro-2H-pyrimido(1,2-a)pyrimidine-N,N')-copper(**I**)]*

F. A. Cotton, X. Feng and D. J. Timmons, *Inorg. Chem.*, 1998, **37**, 4066.

d = 2.89 Å, θ = 131° {centre of inversion}. Copper(I) complex. Binuclear and centrosymmetric complex. Molecules associate into a linear supramolecular chain *via* N-methylene-H interactions.

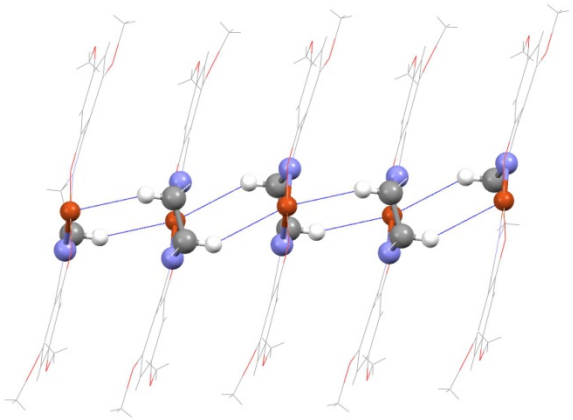


PYCICU

(Pyrrole-2-(N-3-propanolato)-carboxaldimino)copper(II)

J. A. Bertand and C. E. Kirkwood, *Inorg. Chim. Acta*, 1972, **6**, 248.

d = 2.86 Å, θ = 132° {centre of inversion}. Binuclear and centrosymmetric complex with imine groups. Molecules associate into a linear supramolecular chain *via* imine-methylene-H interactions.

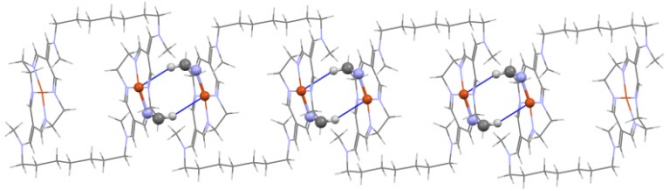


VUYHUT

(3,3',5,5'-Tetramethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato)-copper(II)

G. Assey, R. J. Butcher and Y. Gultneh, *Acta Crystallogr. Sect. E: Struct. Rep. Online,* 2010, **66**, m653.

d = 2.77 Å, θ = 143°; *d* = 2.90 Å, θ = 142°. Schiff base complex with ethylene bridge. Each methylene group (anti disposition) forms a methylene-H interaction leading to a supramolecular linear chain.

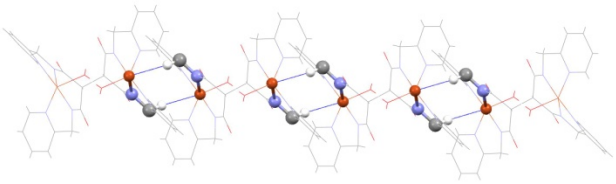


WEGKID

(μ_2-3,11,15,18,22,30,34,37,40,43,46,49-Dodeca-aza-3,11,22,30-tetramethyltricyclo-(30.6.6.6^{12,19})pentaconta-1,12,14,18,20,31,33,37,39,43,45,49-dodecaene)-di-copper tetrakis(hexafluorophosphate) tetrahydrate

S. Domagała, A. Więckowska, J. Kowalski, A. Rogowska, J. Sydłowska, B. K. Daszkiewicz, R. Bilewicz and K. Woźniak, *Chem. Eur. J.*, 2006, **12**, 2967.

d = 2.79 Å, θ = 158° {centre of inversion}. Centrosymmetric oligomer encompassing two macrocycles with two imine groups. A methylene-H from each macrocycle forms an interaction leading to a linear supramolecular chain. Nickel complex {**WEGLEA**} associates in a similar fashion.

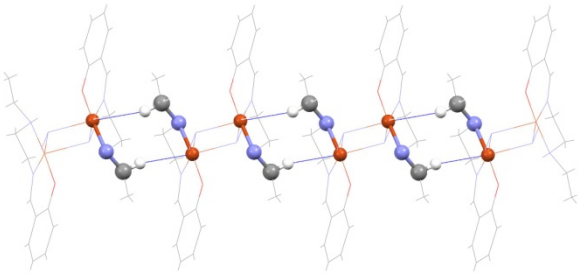


WUGLUG

(μ_2-1,1,2,2-tetrakis((Pyridin-2-ylmethyl)carbamoyl)ethane)-diaqua-di-copper(II) decahydrate

F. A. Mautner, E. R. Taylor, D. M. Rozas and S. S. Massoud, *J. Mol. Struct*., 2009, **936**, 250.

d = 2.65 Å, θ = 167° {centre of inversion}. Binuclear and centrosymmetric complex. Molecules associate into a linear supramolecular chain *via* R_2N-methylene-H interactions.



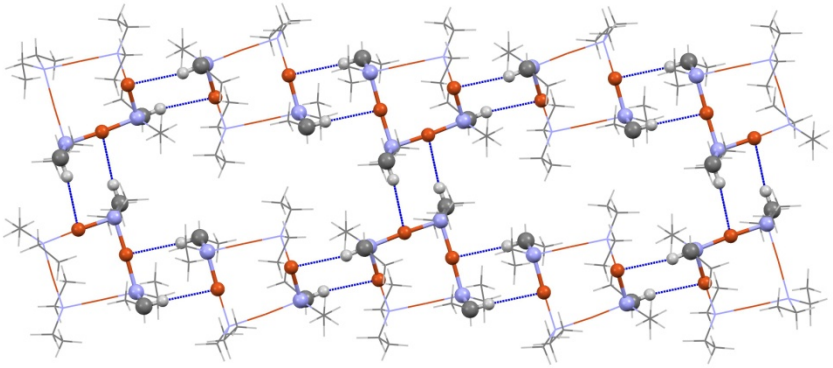
YADGUG

Bis[(μ_2-Azido-N,N)-(N-(2-(ethylamino)ethyl)salicyaldiminato)-copper(II)]

M. S. Ray, A. K. Ghosh, S. Chaudhuri, M. G. B. Drew and J. Ribas, *Eur. J. Inorg. Chem*., 2004, 3110.

d = 2.80 Å, θ = 164° {centre of inversion}. Binuclear and centrosymmetric complex with imine groups. Molecules associate into a linear supramolecular chain *via* N-methylene-H interactions involving a terminal N-ethyl group.

TWO-DIMENSIONAL ARRAYS

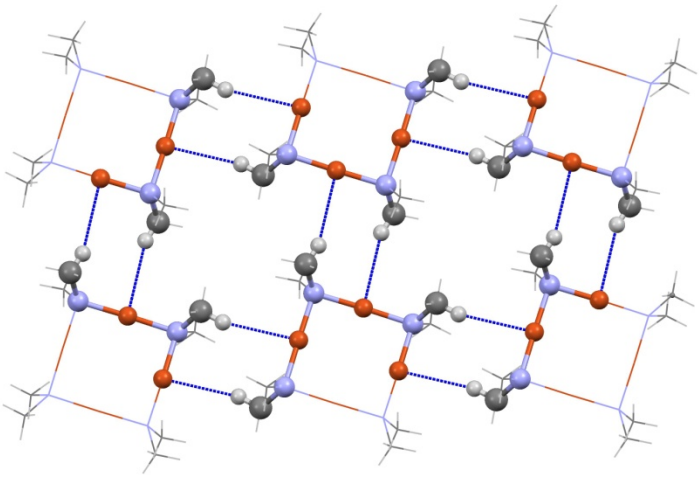


CIDBAS

*tetrakis(Diethylamido)-tetra-copper(**I**)*

H. Hope and P. P. Power, *Inorg. Chem*., 1984, **23**, 936.

d = 2.76 Å, θ = 166° {centre of inversion}. Tetranuclear copper(I) complex with four-fold inversion symmetry and where edges of a copper square are bridged by NEt_2. A two-dimensional array arises from methylene-H interactions.

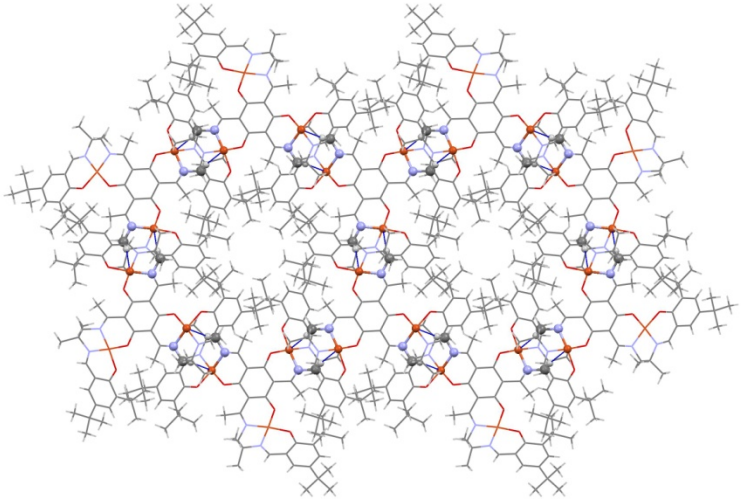


FIMYAB

*Cyclo-tetrakis[(μ_2-N,N-dimethylamino-N,N)-copper(**I**)]*

S. Gambarotta, M. Bracci, C. Florini, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc. Dalton Trans*., 1987, 1883.

d = 2.85 Å, θ = 155°; d = 2.92 Å, θ = 160°. Tetranuclear copper(I) complex with inversion symmetry and where edges of a copper square are bridged by NMe_2. A two-dimensional array arises from methyl-H interactions.



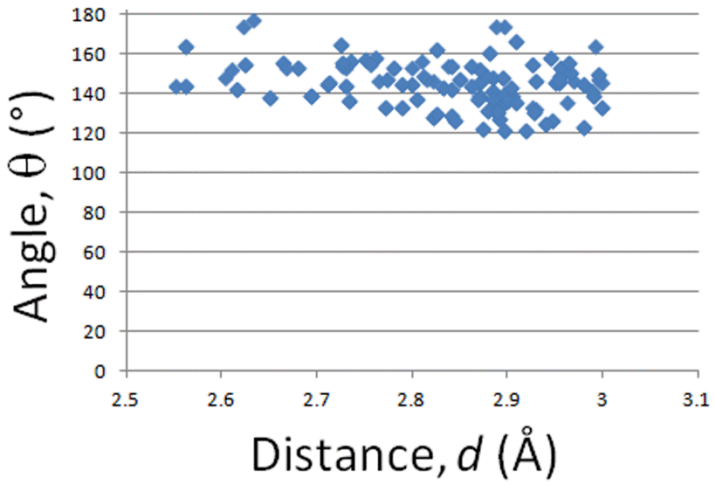
HIWSAI

(μ_3-2,4,6-tris(1-(2-(3,5-Di-t-butylsalicylideneamino)-2-methylpropylimino)-ethyl)benzene-1,3,5-triolato)-tri-copper(II) chloroform solvate

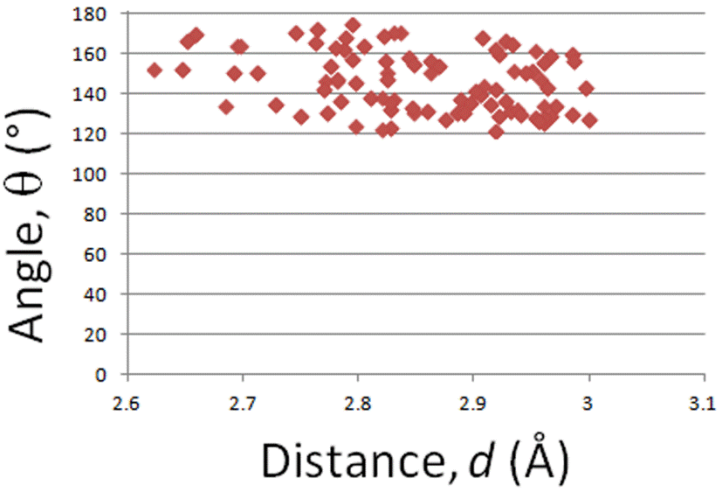
T. Glaser, M. Heidemeier, J. B. H. Strautmann, H. Bogge, A. Stammier, E. Krickemeyer, R. Huenerbein, S. Grimme, E. Bothe and E. Bill, *Chem. Eur. J.*, 2007, **13**, 9191.

d = 2.66 Å, θ = 170° {centre of inversion}. Trinuclear complex with three Schiff base residues, with (dimethyl)ethylene bridges, cleaved onto a central benzene ring – three-fold symmetry. One methylene-H from each forms an interaction to generate a two-dimensional array. The nickel complex {**WAQVEQ**} forms a similar arrangement.

Figure S(1). Plots of distance, d (Å) versus angle, θ (°) for (a) nickel complexes and (b) copper complexes.



(a)



(b)