

Investigations of Putative arene-C–H... π (quasi-chelate ring) Interactions in Copper(I) Structures†

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Electronic Supplementary Information

Details of synthesis and characterisation

Instrumentation and materials

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 solution on a Bruker Avance 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane as internal reference. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 solution on the same instrument but with the chemical shifts recorded relative to 85% aqueous H_3PO_4 as external reference; abbreviations for NMR assignments: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *sept*, septet; *m*, multiplet. IR spectra were measured on a Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer in the range 4000 to 400 cm^{-1} . Elemental analyses were performed on a Perkin Elmer PE 2400 CHN Elemental Analyser. Melting points were determined on a Krüss KSP1N melting point meter. All reactions were carried out under ambient conditions. All chemicals and solvents were sourced commercially and used as received.

Synthesis

Preparation of $(\text{Ph}_3\text{P})_2\text{CuCl}\{\text{MeOC}(=\text{S})\text{N}(\text{H})\text{Ph}\}$ (**1**)

To CuCl (2.5 mmol, 0.25 g) in acetonitrile (25 ml) was added an equimolar quantity of $\text{MeOC}(=\text{S})\text{NHPH}$ (0.42 g) in acetonitrile (25 ml), followed by addition of two mole equivalent of triphenylphosphane (5.0 mmol, 1.31 g) also in acetonitrile (25 mL). The resulting mixture was stirred for 3 h at 50 °C, giving a white suspension. An equal volume of dichloromethane (75 ml) was added to the suspension and the clear solution that resulted was left for slow evaporation at room temperature, yielding colourless crystals after 1 week. This procedure was also used to prepare **2** and **3** using the appropriate thiocarbamide precursor.

Spectroscopic characterisation

(Ph₃P)₂Cu[MeOC(=S)N(H)Ph]Cl (1)

Yield: 1.898 g (96 %), colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 11.86 (*s*, br, 1H, NH), 7.45 – 7.16 (*m*, br, 35H, Ph₃P, aryl-H), 3.96 (*s*, 3H, OCH₃) ppm. ¹³C{¹H} NMR (400 MHz, CDCl₃, 25 °C): δ 186.7 (Cq), 137.5 (Ph, C1), 134.4 (d, *m*-PC₆H₅, J_{CP} = 58.5 Hz), 133.9 (d, *i*-PC₆H₅, J_{CP} = 99.2 Hz), 129.4 (*s*, *p*-PC₆H₅), 128.7 (Ph, C3), 128.4 (d, *o*-PC₆H₅, J_{CP} = 35.8 Hz), 125.1 (Ph, C2), 121.9 (Ph, C4), 58.2 (OCH₃) ppm. ³¹P{¹H}NMR (400 MHz, CDCl₃, 25 °C): δ -4.0 ppm. Anal. Calc. for C₄₄H₃₉ClCuNOP₂S: C, 66.83; H, 4.97; N, 1.77%. Found: C, 66.92; H, 4.81; N, 1.77%. IR: 3052(w) ν(N–H), 1434(s) ν(C–N), 1219(s) ν(C=S), 1094(s) ν(C–O). M.pt: 160-161 °C.

(Ph₃P)₂Cu[EtOC(=S)N(H)Ph]Cl (2)

Yield: 1.891 g (94 %), colourless crystals. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 11.81 (*s*, br, 1H, NH), 7.42 – 7.16 (*m*, br, 35H, Ph₃P, aryl-H), 4.45 (*q*, 2H, OCH₂, J = 7.08 Hz), 1.29 (*t*, 3H, CH₃, J = 7.08 Hz) ppm. ¹³C{¹H} NMR (400 MHz, CDCl₃, 25 °C): δ 185.7 (Cq), 137.7 (Ph, C1), 133.9 (d, *m*-PC₆H₅, J_{CP} = 58.9 Hz), 133.9 (d, *i*-PC₆H₅, J_{CP} = 95.0 Hz), 129.3 (*s*, *p*-PC₆H₅), 128.7 (Ph, C3), 128.3 (d, *o*-PC₆H₅, J_{CP} = 34.7 Hz), 124.9 (Ph, C2), 121.8 (Ph, C4), 68.1 (OCH₂), 14.1 (CH₃) ppm. ³¹P{¹H} NMR (400 MHz, CDCl₃, 25 °C): δ -4.1 ppm. Anal. Calc. for C₄₅H₄₁ClCuNOP₂S: C, 67.16; H, 5.14; N, 1.74%. Found: C, 67.51; H, 5.01; N, 1.77%. IR: 3054(w) ν(N–H), 1433(s) ν(C–N), 1225(s) ν(C=S), 1093(s) ν(C–O). M.pt: 163-166 °C.

(Ph₃P)₂Cu[iPrOC(=S)N(H)Ph]Cl (3)

Yield: 1.904 g (93 %), colourless crystals. ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ 11.86 (s, br, 1H, NH), 7.41 – 7.15 (m, br, 35H, Ph_3P , aryl-H), 5.46 (sept, 1H, OCH, $J = 6.13\text{Hz}$), 1.24 (d, 6H, CH_3 , $J = 6.16\text{Hz}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 25 °C): δ 184.8 (Cq), 137.8 (Ph, C1), 133.9 (d, *m*- PC_6H_5 , $J_{\text{CP}} = 59.1\text{ Hz}$), 133.9 (d, *i*- PC_6H_5 , $J_{\text{CP}} = 95.1\text{ Hz}$), 129.3 (s, *p*- PC_6H_5), 128.7 (Ph, C3), 128.3 (d, *o*- PC_6H_5 , $J_{\text{CP}} = 35.5\text{ Hz}$), 124.8 (Ph, C2), 121.8 (Ph, C4), 76.3 (OCH), 21.7 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 25 °C): δ -4.3 ppm. Anal. Calc. for $\text{C}_{46}\text{H}_{43}\text{ClCuNOP}_2\text{S}$: C, 67.48; H, 5.29; N, 1.71%. Found: C, 67.79; H, 4.91; N, 1.84%. IR: 3048(w) $\nu(\text{N-H})$, 1433(s) $\nu(\text{C-N})$, 1225(s) $\nu(\text{C=S})$, 1093(s) $\nu(\text{C-O})$. M.pt: 169-173 °C.

X-ray crystallography

Intensity data for **1–3** were measured at 100 K on an Agilent Technologies SuperNova Dual CCD with an Atlas detector fitted with MoK α radiation ($\lambda = 0.71073$ Å) to $\theta_{\max} = 27.5^\circ$. Data processing and absorption correction were accomplished with CrysAlis PRO.¹ The structures were solved by direct methods with SHELXS-97² and refinement (anisotropic displacement parameters, C-bound hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ for $P = (F_o^2 + 2F_c^2)/3$) was on F^2 by means of SHELXL-97.² The molecular structure diagrams were drawn with ORTEP-3 for Windows³ at the 70% probability level, the overlap diagram was drawn with QMol⁴ and the remaining crystallographic figures were drawn with DIAMOND⁵ using arbitrary spheres. Data manipulation and interpretation were with WinGX³ and PLATON.⁶ Crystal data and refinement details are given in ESI Table S(1).

Computational details

The calculations were performed with Gaussian09⁷ and used the BP86,⁸ B3LYP,⁹ M06-2X¹⁰ and B3PW91¹¹ functionals including the D3 version of Grimme's dispersion correction,¹² and MP2¹³ theory. In all calculations, the def2-TZVP basis set was employed.¹⁴ The model complex **4'** without all phenyl rings, and acetylene were fully optimized at BP86-D.

The isotropic NICS values were calculated using the gauge-including atomic orbitals (GIAO)¹⁵ method using the BP86, B3LYP and B3PW91 functionals. "Dummy" atoms were included at 0.0 Å (NICS(0)), 1.0 Å above (NICS(1)), and -1.0 Å below the centroid (Ω) of the quasi-chelate ring. The molecular orbitals were plotted using an isovalue = 0.02 at BP86-D/def2-TZVP.

The interaction energies for C–H... π (CuCl...HNCS) were estimated by using the C₂H₂...4' model system, removing the basis set superposition error (BSSE) by counterpoise (CP) correction. Single point calculations have been done employing different theories (B3LYP-D, BP86-D, M062X-D, and MP2) using the fully optimized geometries of acetylene and 4'. The $r(\text{H}\dots\Omega)$ distances ranged from 2.2 to 3.0 Å, for three positions in the ring ($\Omega_1 = 0$ Å, $\Omega_2 = 0.920$ Å, and $\Omega_3 = 1.74$ Å starting from the centroid to the S atom); see ESI Figure S8.

The NCI analysis was performed using the NCIPLOT (version 3) program,¹⁶ using the default value for all parameters, including the reduced density gradient ($s = 0.5$) and electron density ($\rho = 0.05$).

References:

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ESI Table S(1) Crystal data and refinement details for **1–3**

Compound	(1)	(2)	(3)
Formula	C ₄₄ H ₃₉ ClCuNOP ₂ S	C ₄₅ H ₄₁ ClCuNOP ₂ S	C ₄₆ H ₄₃ ClCuNOP ₂ S
Formula weight	790.75	804.78	818.80
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P2</i> ₁ / <i>c</i>
<i>a</i> /Å	43.7273(13)	10.1419(3)	16.3060(8)
<i>b</i> /Å	9.6943(3)	13.0254(5)	9.7632(5)
<i>c</i> /Å	19.2365(4)	15.2772(3)	25.6601(15)
α /°	90	84.350(3)	90
β /°	105.830(4)	76.690(2)	91.484(5)
γ /°	90	84.824(3)	90
<i>V</i> /Å ³	7845.2(4)	1949.64(10)	4083.7(4)
<i>Z</i>	8	2	4
<i>D</i> _x /g cm ⁻³	1.339	1.371	1.332
μ (MoK α)/mm ⁻¹	0.795	0.801	0.766
<i>F</i> (000)	3280	836	1704
Crystal size/mm	0.10 x 0.10 x 0.40	0.25 x 0.25 x 0.30	0.10 x 0.10 x 0.20
Reflections collected	62312	16666	39600
Independent/observed	9006	8958	9376
reflections with <i>I</i> > 2 σ (<i>I</i>)	7076	7635	6946
No. of parameters	464	473	483
<i>a</i> , <i>b</i> in weighting scheme	0.024, 12.846	0.038, 1.008	0.022, 2.749
Final <i>R</i> and <i>wR</i> ₂ (obs. data)	0.039, 0.078	0.034, 0.079	0.044, 0.080
Final <i>R</i> and <i>wR</i> ₂ (all data)	0.057, 0.088	0.044, 0.086	0.071, 0.094
Largest diff. peak and hole/e Å ⁻³	0.43, -0.42	0.38, -0.45	0.43, -0.46

ESI Table S(2) Geometric parameters (Å, °) characterising the intramolecular N–H...Cl hydrogen bonds in **1–3**

Compound	N1–H1n	H1n...Cl1	N1...Cl1	angle at H1n
(1)	0.869(14)	2.303(14)	3.172(2)	177(2)
(2)	0.872(13)	2.285(13)	3.1546(16)	174.3(18)
(3)	0.878(19)	2.252(19)	3.104(2)	164(2)

ESI Table S(3) Deviations (Å, °) of the constituent non-hydrogen atoms from the least-squares plane through the putative quasi-(CuCl...HNCS) ring, and r.m.s. deviation of the fitted atoms in **1–3**

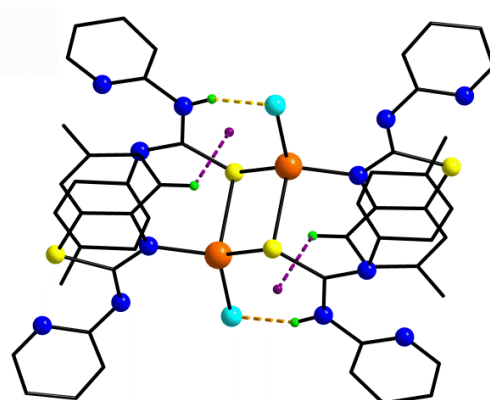
Atom	(1)	(2)	(3)
Plane comprising Cu, Cl1, S1, N1 and C1:			
Cu	0.2633(5)	0.1133(4)	0.0331(5)
Cl1	-0.1811(5)	-0.1039(5)	0.0070(6)
S1	-0.2500(7)	-0.0643(6)	-0.0955(8)
N1	0.1168(11)	0.1286(10)	-0.0917(13)
C1	0.0510(14)	-0.0737(12)	0.1470(16)
r.m.s. deviation	0.1902	0.0997	0.0898
Plane comprising Cl1, S1, N1 and C1:			
Cl1	0.0044(3)	-0.0198(3)	0.0317(4)
S1	-0.0089(6)	0.0415(6)	-0.0642(7)
N1	-0.0148(10)	0.0680(9)	-0.1095(12)
C1	0.0193(14)	-0.0897(12)	0.1420(16)
r.m.s. deviation	0.0131	0.0608	0.0965
Cu	0.6751(11)	0.3077(11)	0.0909(15)
H1n	0.018(24)	0.096(22)	-0.248(26)

ESI Table S(4) Selected intramolecular geometric parameters (Å, °) for **1–3**

Compound	(1)	(2)	(3)
Cu–Cl1	2.3526(6)	2.3162(5)	2.3247(7)
Cu–S1	2.3514(6)	2.4105(5)	2.3861(7)
Cu–P1	2.2471(6)	2.2792(5)	2.2621(7)
Cu–P2	2.2679(6)	2.2910(5)	2.2774(7)
C1–S1	1.685(2)	1.6788(19)	1.696(3)
C1–O1	1.331(3)	1.329(2)	1.316(3)
C1–N1	1.331(3)	1.333(2)	1.331(3)
Cl1–Cu–S1	109.92(2)	107.830(18)	108.51(2)
Cl1–Cu–P1	106.59(2)	109.621(18)	107.27(3)
Cl1–Cu–P2	104.27(2)	106.318(19)	103.67(3)
S1–Cu–P1	102.36(2)	104.020(18)	113.57(3)
S1–Cu–P2	105.88(2)	102.733(18)	99.96(2)
P1–Cu–P2	127.25(2)	125.099(19)	122.86(3)
Cu–S1–C1	109.85(8)	114.00(6)	112.14(9)
S1–C1–O1	123.22(18)	122.96(14)	124.78(18)
S1–C1–N1	122.33(18)	123.22(14)	121.69(19)
O1–C1–N1	114.44(19)	113.81(16)	113.5(2)

ESI Table S(5). Diagrams and geometric details of intramolecular C–H... π (CuCl...HNCS) interactions. Molecules 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 for reasons of clarity, as are non-participating hydrogen atoms.

1 CINPOF



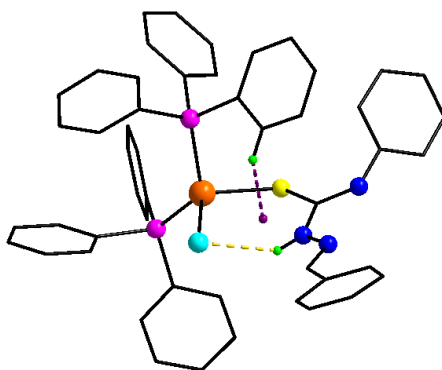
Bis[μ_2 -1-(Pyridin-2-yl)-3-(p-tolyl)thiourea]-bis(N-(6-methylbenzothiazol-2-yl)-N-(pyridin-2-yl)amine]-dichloro-di-copper(I) chloroform solvate

J. T. Lenthall, K. M. Anderson, S. J. Smith and J.W. Steed, *Cryst. Growth Des.*, 2007, 7, 1858.

$d = 2.80 \text{ \AA}$, $\alpha = 114^\circ$. There are two independent and centrosymmetric binuclear molecules in the asymmetric unit, one of these forms two arene-C–H... π (quasi-chelate) interactions.

Deviations from the least-squares plane: Cu -0.078(4), Cl 0.026(10), S 0.122(7), N 0.05(3) and C -0.12(4) \AA . RMS deviation = 0.0878 \AA .

2 ELIROH



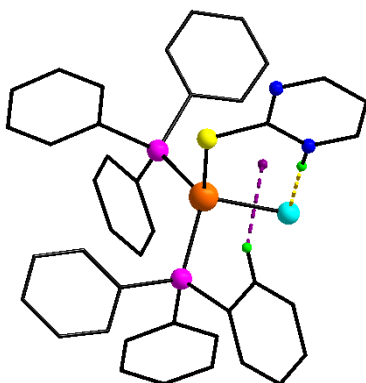
(2-Benzylidene-N-phenylhydrazinecarbothioamide)-chlorobis(triphenylphosphine)-copper(I) acetonitrile solvate

T. S. Lobana, R. Sharma, A. Castiñeras and R. J. Butcher, *Z. Anorg. Allg. Chem.*, 2010, **636**, 2698.

$d = 2.50 \text{ \AA}$, $\alpha = 126^\circ$. Arene-C-H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu -0.0894(8), Cl 0.0289(16), S 0.1615(16), N 0.081(5) and C -0.182(6) \AA . RMS deviation = 0.1221 \AA .

3 IWOSES



Chloro-(pyrimidine-2(1H)-thione-S)-bis(triphenylphosphine)-copper(I)

D. Li, W-J. Shi, T. Wu and S. W. Ng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, m776.

$d = 2.78 \text{ \AA}$, $\alpha = 131^\circ$. Arene-C-H... π (quasi-chelate) interaction.

IWOSES01: T. S. Lobana, P. Kaur, A. Castiñeras, P. Turner and T. W. Failes, *Struct. Chem.*, 2008, **19**, 727.

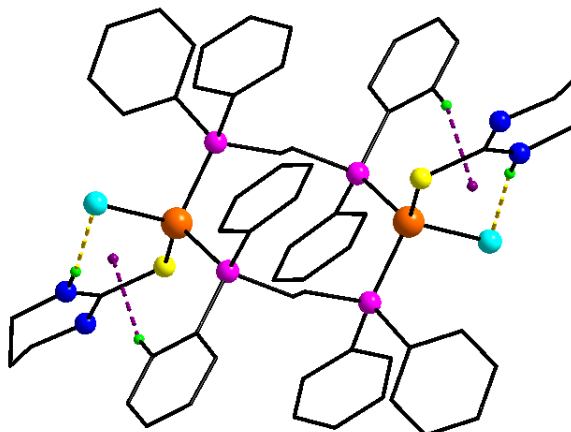
$d = 2.72 \text{ \AA}$, $\alpha = 131^\circ$. Arene-C-H... π (quasi-chelate) interaction.

IWOSES01: N. J. M. Sanghamitra, M. K. Adwankar, A. S. Juvekar, V. Khurajjam, C. Wycliff and A. G. Samuelson, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 2011, **50**, 465.

$d = 2.77 \text{ \AA}$, $\alpha = 131^\circ$. Arene-C-H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu -0.0443(3), Cl 0.0459(7), S 0.018(7), N -0.066(2) and C 0.046(2) \AA . RMS deviation = 0.0466 \AA (IWOSES)

4 JAJVAS

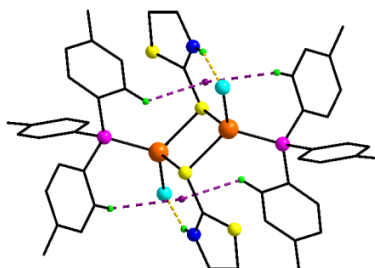


Bis[μ_2 -trans-1,2-bis(Diphenylphosphino)ethene)-dichlorobis(tetrahydropyrimidine-2-thione)]-dicopper(I)

P. Aslanidis, P. J. Cox, S. Divanidis and P. Karagiannidis, *Inorg. Chim. Acta*, 2004, **357**, 4231.
 $d = 2.59 \text{ \AA}$, $\alpha = 156^\circ$. There are two independent and centrosymmetric tetranuclear molecules in the asymmetric unit. One of these features two arene-C–H... π (quasi-chelate) interactions.

Deviations from the least-squares plane: Cu 0.1951(4), Cl -0.1534(7), S -0.1423(8), N 0.151(2) and C -0.050(2) \AA . RMS deviation = 0.1464 \AA .

5 JITFOH



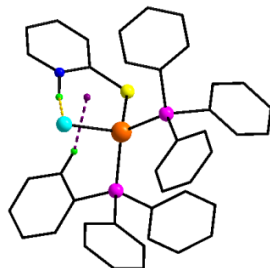
Bis[$(\mu_2$ -1,3-Thiazolidine-2-thionato)-chloro-tri-p-tolylphosphine-copper(I)]

S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, D. Mentzafos and A. Terzis, *Polyhedron*, 1991, **10**, 935.

$d = 2.68 \text{ \AA}$, $\alpha = 125^\circ$; $d = 2.78 \text{ \AA}$, $\alpha = 121^\circ$. Centrosymmetric molecule with four arene-C–H... π (quasi-chelate) interactions as each ring accepts two of these.

Deviations from the least-squares plane: Cu -0.0606(3), Cl 0.0784(6), S -0.0173(6), N -0.155(3) and C 0.154(3) \AA . RMS deviation = 0.1076 \AA .

6 KAJPUG



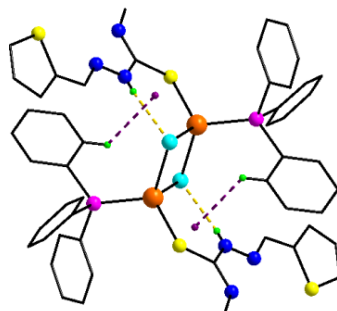
Chloro-(2(1*H*)-pyridinethione-*S*)-bis(triphenylphosphine)-copper(I)

T. S. Lobana, P. K. Bhatia and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1989, 749.

$d = 2.65 \text{ \AA}$, $\alpha = 131^\circ$. Arene-C-H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu 0.0441(10), Cl -0.044(2), S -0.019(3), N 0.063(7) and C -0.044(8) \AA . RMS deviation = 0.0451 \AA .

7 KUGTEM



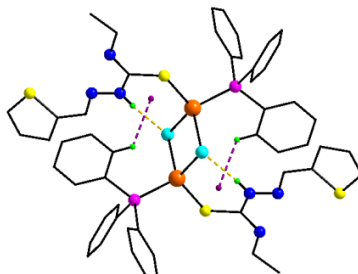
bis(μ_2 -Chloro)-bis(N-methyl-2-(2-thienylmethylene)hydrazinecarbothioamide)-bis(triphenylphosphine)-di-copper(I)

T. S. Lobana, R. Sharma, A. Castiñeiras, G. Hundal and R. J. Butcher, *Inorg. Chim. Acta*, 2009, **362**, 3547.

$d = 2.90 \text{ \AA}$, $\alpha = 115^\circ$. Centrosymmetric molecule featuring two arene-C-H... π (quasi-chelate) interactions.

Deviations from the least-squares plane: Cu 0.0085(6), Cl -0.0169(12), S 0.0127(14), N 0.042(5) and C -0.046(5) \AA . RMS deviation = 0.0297 \AA .

8 KUGTUC



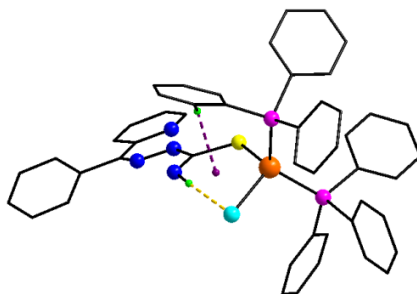
Bis(μ_2 -chloro)-bis(N-ethyl-2-(2-thienylmethylene)hydrazinecarbothioamide)-bis(triphenylphosphine)-di-copper(I)

T. S. Lobana, R. Sharma, A. Castiñeiras, G. Hundal and R. J. Butcher, *Inorg. Chim. Acta*, 2009, **362**, 3547.

$d = 2.92 \text{ \AA}$, $\alpha = 115^\circ$. Centrosymmetric molecule featuring two arene-C–H... π (quasi-chelate) interactions.

Deviations from the least-squares plane: Cu -0.0022(3), Cl -0.0110(8), S 0.0257(10), N 0.041(2) and C -0.054(3) \AA . RMS deviation = 0.0328 \AA .

9 QUGNIQ



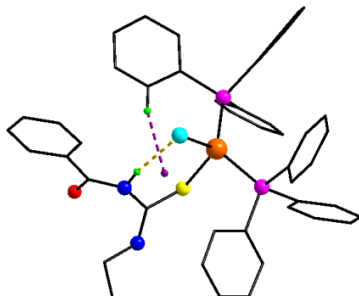
Chloro-(2-(phenyl(pyridin-2-yl)methylene)hydrazinecarbothioamide)-bis(triphenylphosphine)-copper(I) acetonitrile solvate

T. S. Lobana, S. Khanna, G. Hundal, R. J. Butcher and A. Castiñeiras, *Polyhedron*, 2009, **28**, 3899.

$d = 2.56 \text{ \AA}$, $\alpha = 134^\circ$. Arene-C–H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu -0.1830(4), Cl 0.1637(9), S 0.1040(8), N -0.205(3) and C 0.121(3) \AA . RMS deviation = 0.1600 \AA .

10 RAJREB



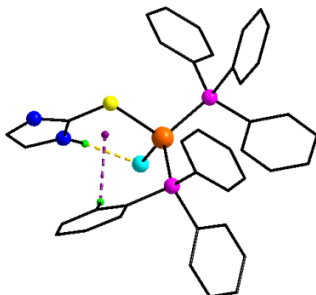
Chloro-bis(triphenylphosphine)-(N-diethyl(carbamothioyl)benzamide)-copper(I)

N. Gunasekaran, P. Ramesh, M. N. G. Ponnuswamy and R. Karvembu, *Dalton Trans.*, 2011, **40**, 12519.

$d = 2.54 \text{ \AA}$, $\alpha = 163^\circ$. Arene-C–H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu 0.0170(4), Cl 0.0394(11), S -0.1415(11), N -0.181(3) and C 0.266(4) \AA . RMS deviation = 0.1584 \AA .

11 TIZRAW



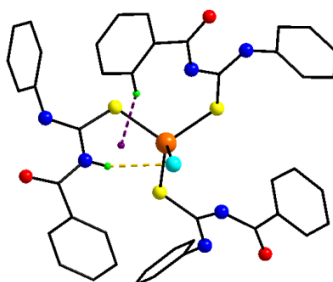
Chloro-bis(triphenylphosphine)-(imidazoline-2-thionato)-copper(I) chlorobis(triphenylphosphine)-copper(I) methanol solvate

T. S. Lobana, R. Sultana and G. Hundal, *Polyhedron*, 2008, **27**, 1008.

$d = 2.53 \text{ \AA}$, $\alpha = 128^\circ$. There are two independent molecules in the asymmetric unit and one of these features an arene-C–H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu -0.1650(3), Cl 0.1035(10), S 0.1964(9), N -0.023(3) and C -0.112(3) \AA . RMS deviation = 0.1339 \AA .

12 TUKDEJ



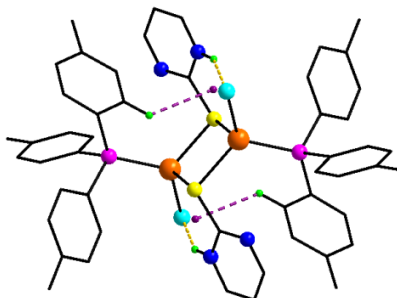
Chloro-tris(1-phenyl-3-benzoylthiourea-S)-copper(I)

M. K. Rauf, Imtiaz-ud-Din, A. Badshah, M. Gielen, M. Ebihara, D. de Vos and S. Ahmed, *J. Inorg. Biochem.*, 2009, **103**, 1135.

$d = 2.82 \text{ \AA}$, $\alpha = 156^\circ$. Arene-C–H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu 0.4805(4), Cl -0.3370(10), S -0.3489(9), N 0.305(3) and C -0.100(3) \AA . RMS deviation = 0.3374 \AA .

13 VIPBIF



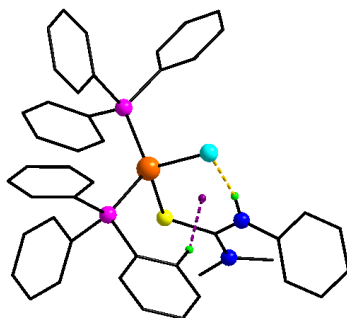
Bis[Chloro-(μ_2 -pyrimidine-2-thionato-S,S)-tri-p-tolylphosphine-copper(I)]

P. Karagiannidis, S. K. Hadjikakou, P. Aslanidis and A. Hountas, *Inorg. Chim. Acta*, 1990, **178**, 27.

$d = 2.63 \text{ \AA}$, $\alpha = 125^\circ$. Centrosymmetric molecule with two arene-C–H... π (quasi-chelate) interactions.

Deviations from the least-squares plane: Cu -0.0328(3), Cl 0.0714(6), S -0.0649(6), N -0.1805(16) and C 0.207(3) \AA . RMS deviation = 0.1310 \AA .

14 ZADBOV



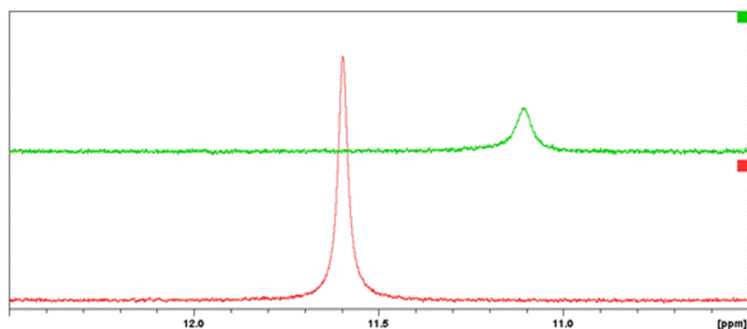
Chloro-(*N,N*-dimethyl-*N'*-phenylthiourea)-bis(triphenylphosphine)-copper(I)

R. Singh and S. K. Dikshit, *Polyhedron*, 1995, **14**, 1799.

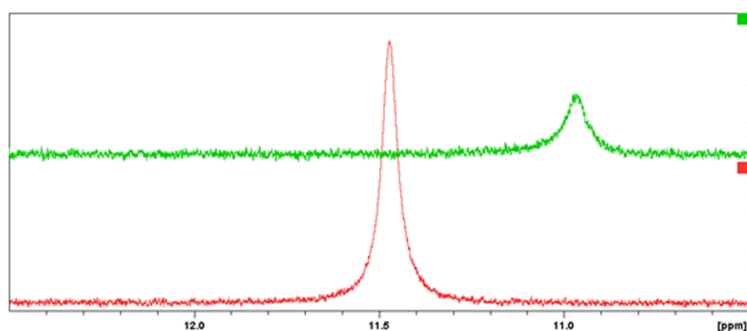
$d = 2.28 \text{ \AA}$, $\alpha = 161^\circ$. Arene-C–H... π (quasi-chelate) interaction.

Deviations from the least-squares plane: Cu -0.0521(5), Cl 0.0505(11), S 0.0273(11), N -0.065(3) and C 0.039(4) \AA . RMS deviation = 0.0485 \AA .

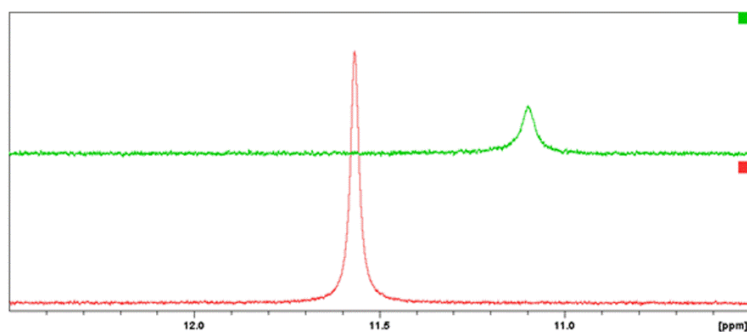
ESI Figure S(1). ^1H NMR spectra for (a) **1**, (b) **2** and (c) **3** measured in CDCl_3 solution at 2.5×10^{-2} M (red spectra) and 2.5×10^{-3} M (green spectra) showing the significant downfield shift in the more concentrated solution, which is correlated with the formation of intramolecular N–H...Cl hydrogen bonds.



(a)

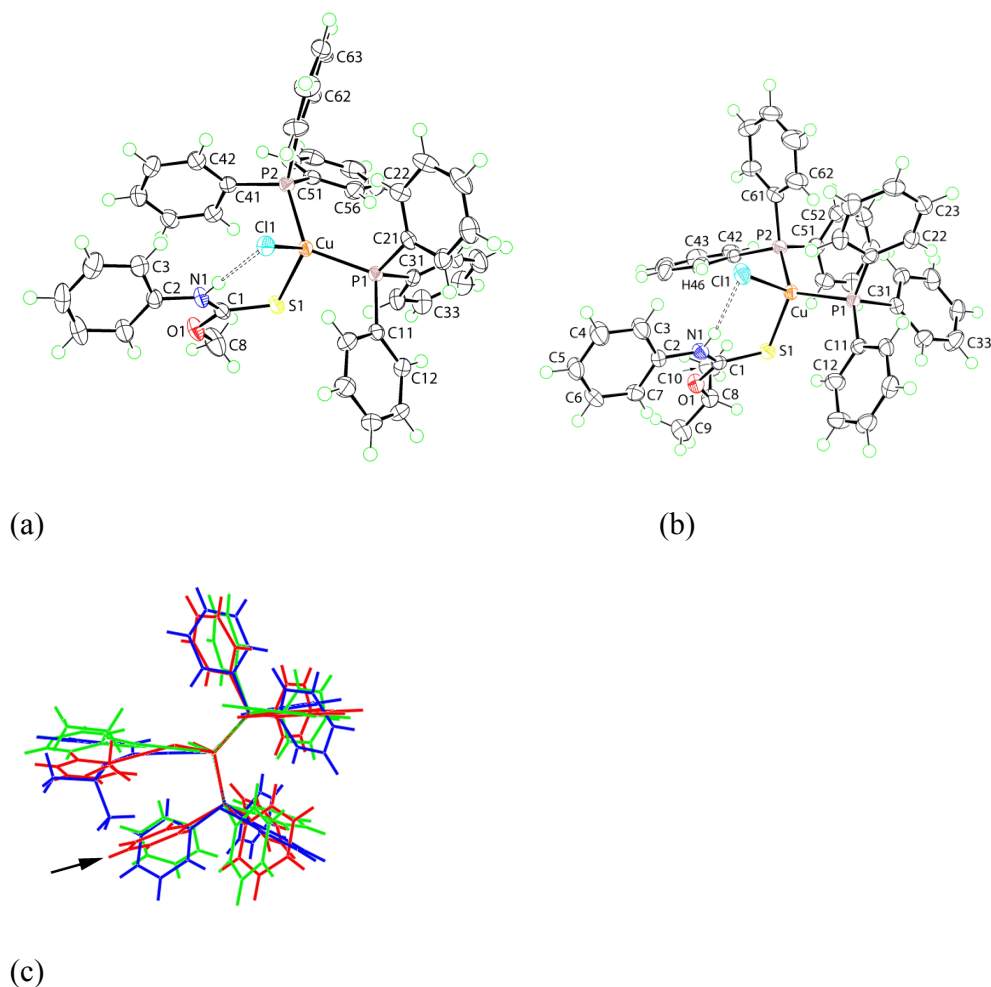


(b)

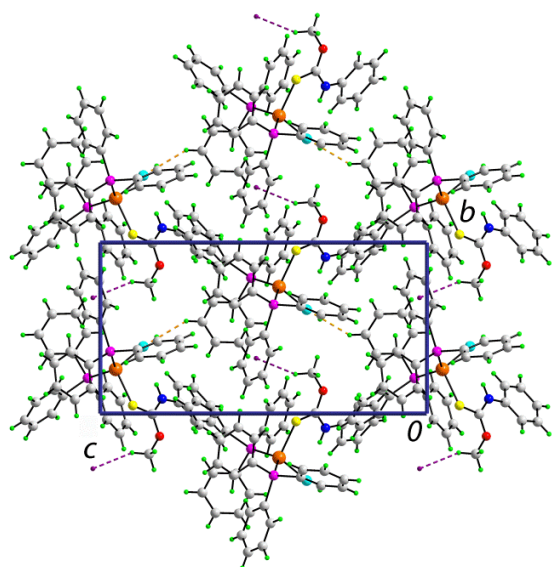


(c)

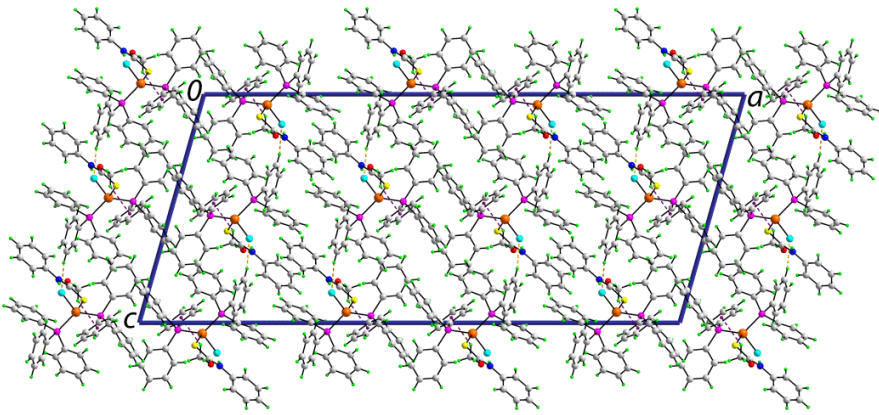
ESI Figure S(2). Molecular structures of (a) **1** and (b) **3**, drawn with 70% displacement ellipsoids and showing atom labelling schemes. (c) Overlay diagram of **1** (red image), **2** (green) and **3** (blue). The molecules have been superimposed so the P1-Cu-P2 atoms are overlapped. In this diagram, the inverted molecule of **2** has been employed for a better fit. The orientation of the overlay diagram has been optimised to highlight the three relevant rings. The arrow indicates the salient rings with regard to putative C–H... π (...ClCuSCNH) interactions with the ring in **1** adopting an almost parallel orientation to the quasi-chelate ring so that no C–H... π (...ClCuSCNH) interaction is formed. For **3**, the C–H46...Cu, Cl1, S1, N1, C1 and H1n separations are 3.17, 2.87, 3.52, 2.99, 3.17 and 2.78 Å, respectively.



ESI Figure S(3). Crystal packing diagrams for **1**: (a) view of the supramolecular layer in the *bc*-plane, and (b) view of the unit cell contents in projection down the *b*-axis. The C–H...Cl [C63–H63...Cl1ⁱ = 2.83 Å, C63...Cl1ⁱ = 3.655(2) Å, with angle at H63 = 146° for symmetry operation *i*: *x*, -*y*, -1/2+*z*] and C–H...π [C8–H8c...Cg(C21–C26)ⁱⁱ = 2.87 Å, C8...Cg(C21–C26)ⁱⁱ = 3.643(3) Å, with angle at H63 = 137° for *ii*: *x*, 1+*y*, *z*] interactions are shown as orange and purple dashed lines, respectively. Phenyl Embraces (PE): P1-phosphane forms a Sextuple PE (SPE) with P...P = 6.89 Å and Cu–P...P angle = 176°. P2-phosphane forms a Parallel Quadruple PE (PQPE) with P...P = 8.72 Å.

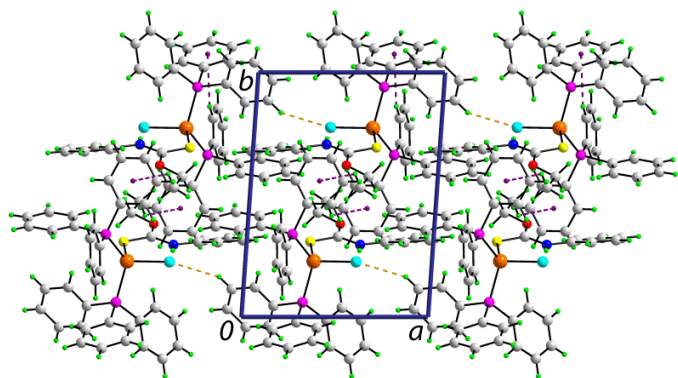


(a)

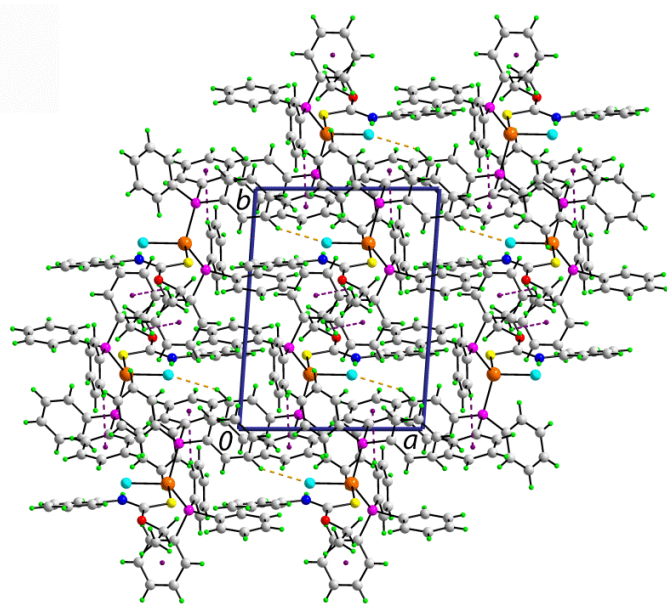


(b)

ESI Figure S(4). Crystal packing diagrams for **2**: (a) view of the supramolecular double chain, and (b) view of the unit cell contents in projection down the *c*-axis. The C–H...Cl [C53–H53...Cl1^{*i*} = 2.74 Å, C53...Cl1^{*i*} = 3.600(2) Å, with angle at H53 = 151° for symmetry operation *i*: 1+*x*, *y*, *z*] and C–H... π [C9–H9c...Cg(C11–C16)^{*ii*} = 2.97 Å, C9...Cg(C11–C16)^{*ii*} = 3.610(3) Å, with angle at H9c = 124° for *ii*: 1-*x*, 1-*y*, 1-*z*; *z*] interactions are shown as orange and purple dashed lines, respectively. Phenyl Embraces (PE): P1-phosphane forms a Sextuple PE (SPE) with P...P = 7.02 Å and Cu–P...P angle = 169°. P2-phosphane forms a Double PE (DPE) with P...P = 8.15 Å.

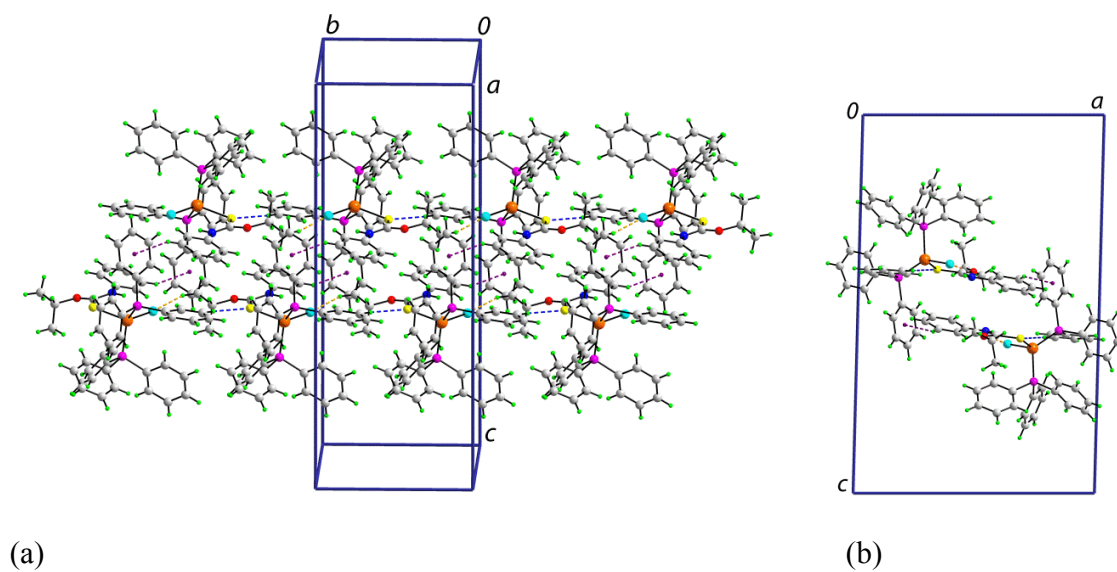


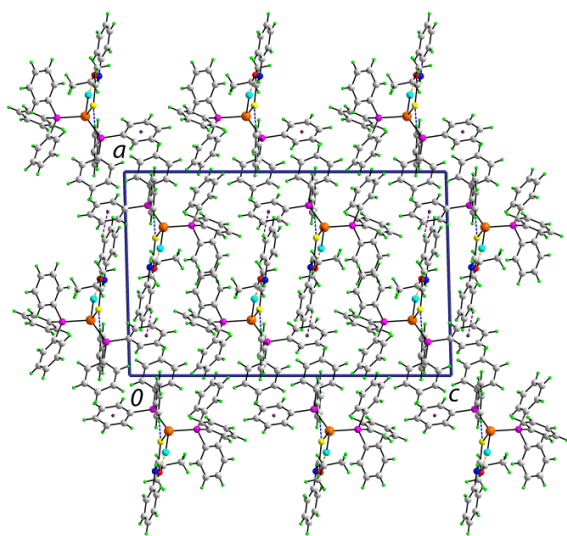
(a)



(b)

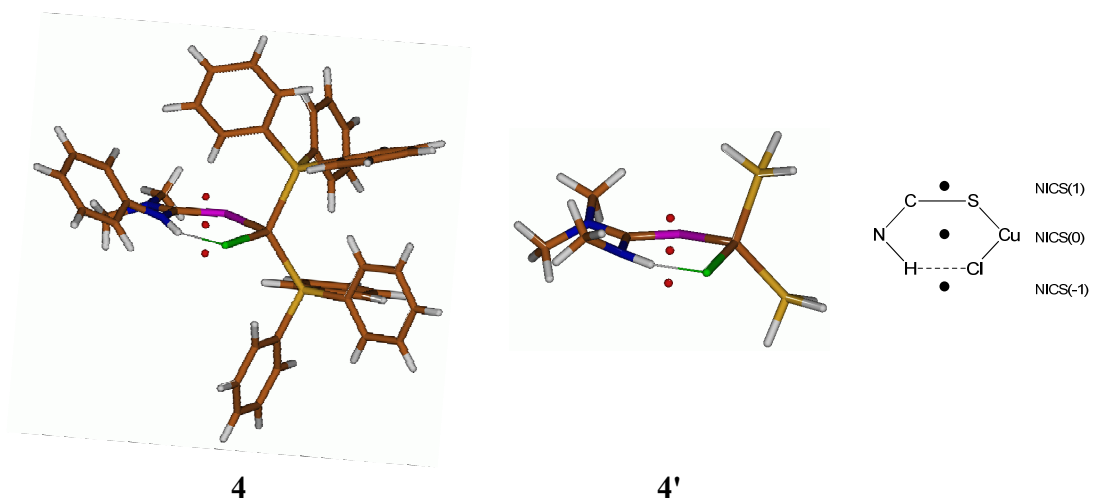
ESI Figure S(5). Crystal packing diagrams for **3**: view of the supramolecular chain, (a) side-on, and (b) down the axis of the tube, and (c) view of the unit cell contents in projection down the *b*-axis. The C–H...Cl [C9–H9b...Cl1ⁱ = 2.66 Å, C9...Cl1ⁱ = 3.547(3) Å, with angle at H9c = 150° for symmetry operation *i*: $x, 1+y, z$], C–H...S [C25–H25...S1ⁱⁱ = 2.79 Å, C25...S1ⁱⁱ = 3.723(3) Å, with angle at H25 = 168° for symmetry operation *ii*: $x, -1+y, z$] and C–H... π [C4–H4...Cg(C11-C16)ⁱⁱⁱ = 2.83 Å, C4...Cg(C11-C16)ⁱⁱⁱ = 3.674(3) Å, with angle at H4 = 149° for *iii*: $1-x, -y, 1-z$] interactions are shown as orange, blue and purple dashed lines, respectively. Phenyl Embraces (PE): P1-phosphane forms a Sextuple PE (SPE) with P...P = 7.10 Å and Cu–P...P angle = 175°. P2-phosphane does not form a recognisable pattern.





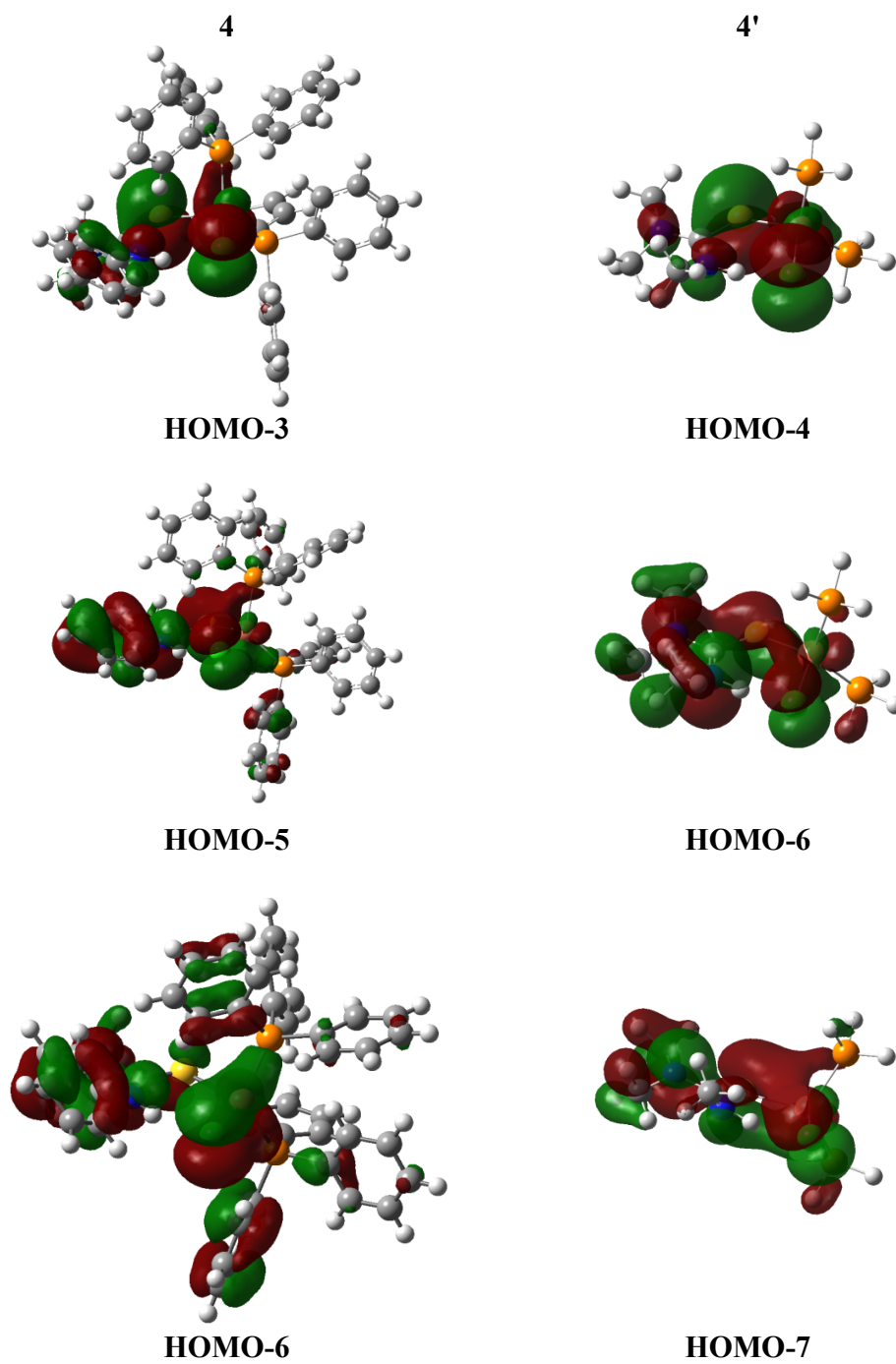
(c)

ESI Figure S(6). NICS(x) (x = -1, 0, 1 in Å) values calculated for **4** and **4'** at the centroid of the quasi-chelate (CuCl...HNCS) ring at DFT/def2-TZVP.

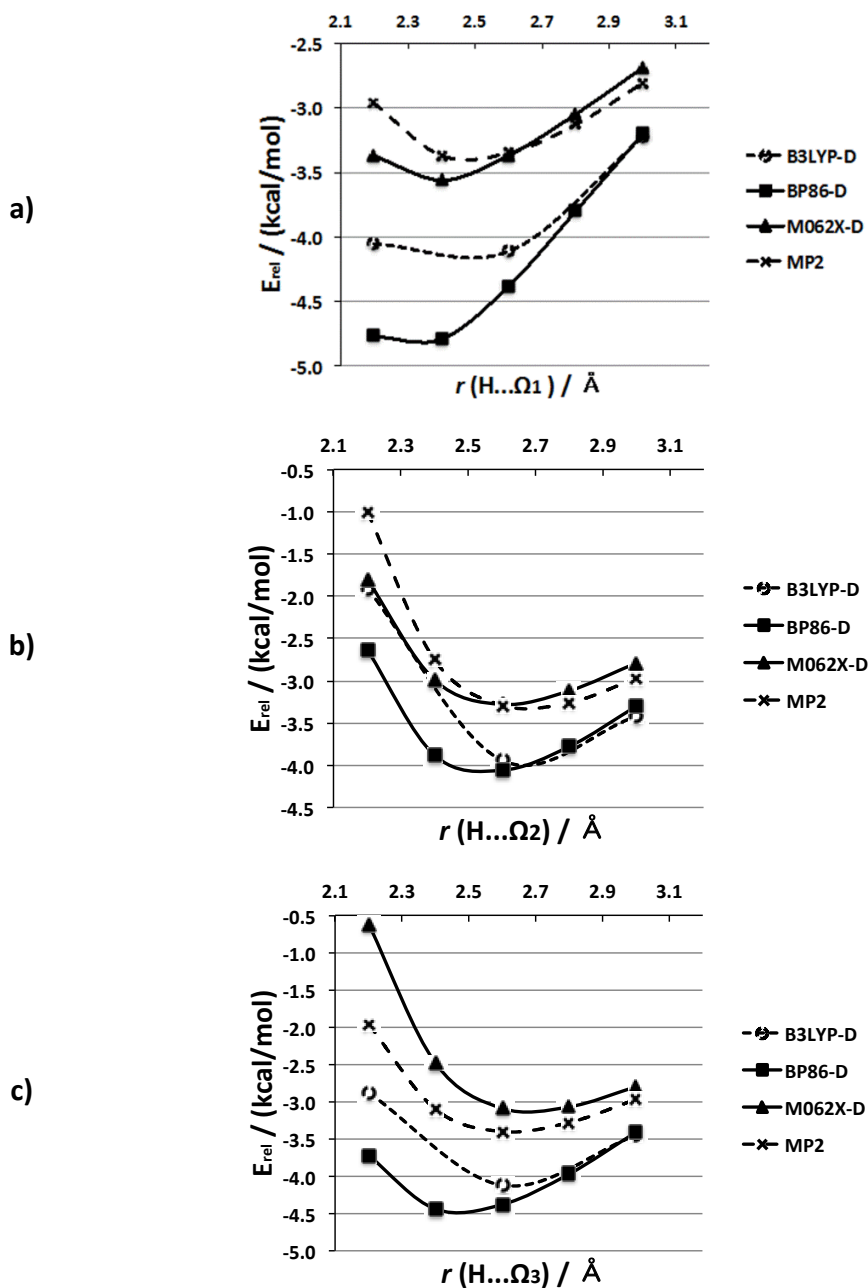


complex	DFT	NICS(-1)	NICS(0)	NICS(1)
4	BP86	0.20	0.32	-1.16
	B3LYP	0.19	0.19	-1.32
	B3PW91	0.20	0.25	-1.27
4'	BP86	0.66	1.85	0.83
	B3LYP	0.60	1.65	0.69
	B3PW91	0.62	1.74	0.73

ESI Figure S(7). Molecular orbitals of **4** and **4'** (BP86-D/def2-TZVP), showing the alignment of the *p*-orbitals of the light-elements comprising the quasi-ring and the *d*-orbital of the Cu atom.



ESI Figure S8: Curves showing the single point energy calculations at different r distances using different theories (B3LYP-D, BP86-D, M062X-D, and MP2 with def2-TZVP basis set: a) $\Omega_1 = 0 \text{ \AA}$, b) $\Omega_2 = 0.920 \text{ \AA}$, and c) $\Omega_1 = 1.74 \text{ \AA}$ related to the centroid. d) Schematic representation of the considered positions involved in the CH... Ω interactions.



d)

