

Electronic Supplementary Material

**Copper(I) complexes of functionalized sulfur-containing ligands:
structural and theoretical insights into chalcogen bonding**

Khodayar Gholivand,^{*a} Samaneh K. Tizhoush,^a Anna Kozakiewicz,^b Kiamars Eskandari^c

and

Kaveh

Farshadfar

^a

Materials and methods

All chemicals and solvents used in the syntheses were commercially available and were used without further purification. IR spectrum was recorded on a Nicolet 510P spectrophotometer using KBr disks. ^1H and ^{13}C NMR spectra were recorded on Bruker (Advance DRS) 300.13 MHz spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

Methods

X-ray crystallography

Orange crystals of **1-4** were obtained from the $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$. The X-ray data for the reported structures were collected at 293(2) K with an Oxford Sapphire CCD diffractometer using Mo K α radiation $\lambda = 0.71073 \text{ \AA}$ and ω -2 θ method. All structures were solved by direct methods and refined with the full-matrix least-squares method on F^2 with the use of SHELX2014 program packages.¹ The analytical absorption corrections were applied (CrysAlis version 171.38.43 package of programs² Rigaku OD., 2015). Positions of hydrogen atoms have been found from the electron density maps and hydrogen atoms were constrained during refinement with the appropriate riding model as implemented in SHELX during refinement. The data collection and refinement processes are summarized in Table S1. The structural data have been deposited at the Cambridge Crystallographic Data Centre: (CCDC No for four structures **1-4** are 1511710, 1511713, 1547975 and 1547974, respectively).

Table S1 Crystal data and structure refinement parameters for **1, 2, 3, and 4**.

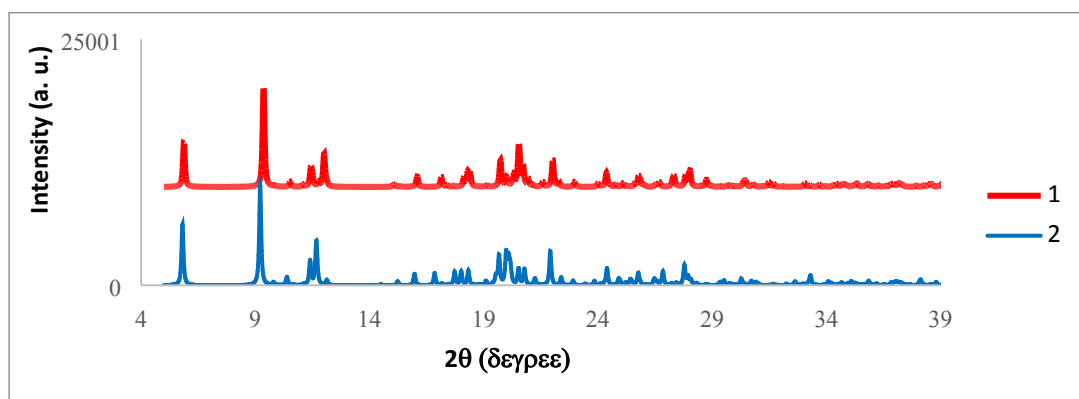
Identification code	1	2	3	4
Empirical formula	$\text{C}_{29}\text{H}_{23}\text{CuN}_5\text{O}_2\text{PS}$	$\text{C}_{29}\text{H}_{23}\text{CuN}_5\text{OPS}_2$	$\text{C}_{24}\text{H}_{18}\text{CuN}_4\text{O}_2\text{PS}_4$	$\text{C}_{24}\text{H}_{18}\text{CuN}_4\text{OPS}_5$
Formula weight, g mol^{-1}	600.09	616.15	617.17	633.23
Crystal size, mm	0.187 x 0.111 x 0.110	0.198 x 0.084 x 0.057	0.439 x 0.311 x 0.025	0.268 x 0.248 x 0.091
Crystal shape, color	needle, orange	plate, orange	plate, orange	plate, orange
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a , \AA	9.8073(7)	9.8681(13)	9.8303(7)	9.7960(15)
b , \AA	10.2949(7)	10.5055(14)	12.5727(12)	12.651(3)
c , \AA	15.0299(8)	15.218(2)	12.6202(12)	12.905(2)
α , deg	89.515(5)	86.886(11)	65.192(9)	63.694(19)
β , deg	89.492(5)	88.725(11)	85.784(7)	84.050(14)
γ , deg	66.462(7)	66.073(13)	71.776(8)	71.894(16)

Volume, Å ³	1391.16(17)	1439.9(4)	1341.8(2)	1361.6(5)
Z, density (calc.), g cm ⁻³	2, 1.433	2, 1.421	2, 1.528	2, 1.545
Absorption coefficient, mm ⁻¹	0.954	0.991	1.215	1.270
F(000)	616	632	628	644
θ range, deg	2.158 to 28.475	2.123 to 28.580	2.186 to 28.467	2.189 to 23.999
Index ranges <i>hkl</i>	-12 ≤ h ≤ 10, -13 ≤ k ≤ 9, -18 ≤ l ≤ 20	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -19 ≤ l ≤ 10	-13 ≤ h ≤ 11, -14 ≤ k ≤ 16, -15 ≤ l ≤ 16	-10 ≤ h ≤ 11, -11 ≤ k ≤ 14, -12 ≤ l ≤ 14
Reflections collected/unique	9539/6160 [R(int)=0.0473]	9897/6391 [R(int)=0.0529]	9712/5947 [R(int) = 0.0528]	7147/4262 [R(int)=0.0814]
Completeness to theta	25.000, 99.5 %	25.000, 99.9 %	25.242, 99.9 %	25.242, 86.6 %
Max and min. transmission	0.885 and 0.779	0.968 and 0.647	0.968 and 0.647	0.885 and 0.779
Data/restraints/parameters	6160 / 0 / 352	6391 / 0 / 352	5947 / 4 / 344	4262 / 0 / 325
Goodness-of-fit on F ²	1.047	1.021	1.000	1.013
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0628, wR2 = 0.1495	R1 = 0.0669, wR2 = 0.1619	R1 = 0.0583, wR2 = 0.1239	R1 = 0.0913, wR2 = 0.2331
R indices (all data)	R1 = 0.1211, wR2 = 0.1886	R1 = 0.1436, wR2 = 0.2435	R1 = 0.1034, wR2 = 0.1492	R1 = 0.1478, wR2 = 0.3017
Residual peaks [eÅ ⁻³]	0.625 and - 0.429	0.495 and -0.626	0.405 and - 0.462	0.922 and -0.729

Table S2 Selected bond length (Å) and angles (°) around copper (I) for complexes **1-4**

1			
Cu1–P1	2.1825(12)	Cu1–N8	2.143(3)
Cu1–N1	2.128(3)	Cu1–N35	1.990(5)
P1–Cu1–N1	119.96(10)	N1–Cu1–N8	77.03(14)
P1–Cu1–N8	125.27(11)	N1–Cu1–N35	100.28(17)
P1–Cu1–N35	120.85(15)	N8–Cu1–N35	103.49(17)
2			
Cu1–P1	2.1928(16)	Cu1–N8	2.159(5)
Cu1–N1	2.139(5)	Cu1–N35	1.984(5)
P1–Cu1–N1	120.36(14)	N1–Cu1–N8	77.05(19)
P1–Cu1–N8	125.94(13)	N1–Cu1–N35	101.0(2)
P1–Cu1–N35	120.31(17)	N8–Cu1–N35	102.58(19)
3			
Cu1–P1	2.2101(11)	Cu1–N8	2.141(3)
Cu1–N1	2.161(3)	Cu1–N41	1.975(4)
P1–Cu1–N1	116.24(9)	N1–Cu1–N8	76.87(13)
P1–Cu1–N8	112.95(10)	N1–Cu1–N41	105.44(14)
P1–Cu1–N41	121.79(10)	N8–Cu1–N41	114.76(13)
4			
Cu1–P1	2.208(3)	Cu1–N8	2.180(8)
Cu1–N1	2.160(8)	Cu1–N41	1.976(9)
P1–Cu1–N1	115.1(2)	N1–Cu1–N8	76.7(3)
P1–Cu1–N8	114.3(2)	N1–Cu1–N41	106.4(3)
P1–Cu1–N41	122.8(2)	N8–Cu1–N41	112.2(3)

(a)



(b)

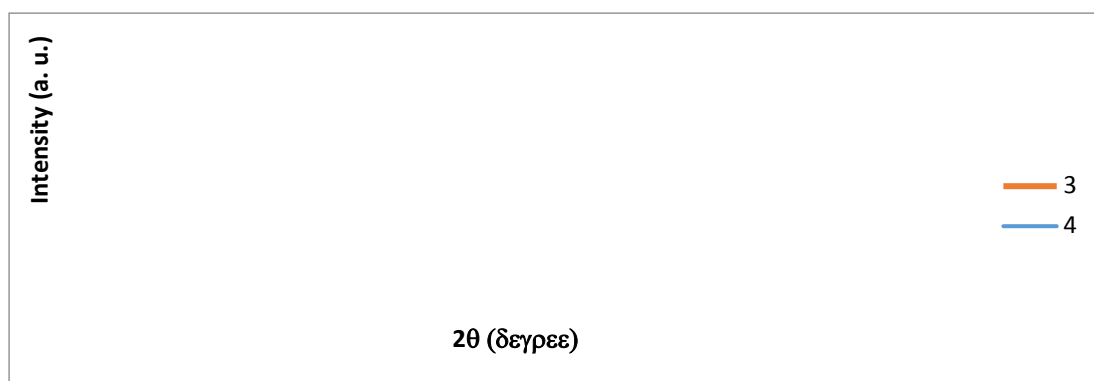


Figure S1 Simulated PXRD pattern of **1** and **2** (a), **3** and **4** (b) calculated from single-crystal data.

Table S3 Similarity index of structures

complex	Dimensionality	Dissimilarity index (X)	Stretch Parameter (D)/ Å	Δ^α (angles, deg)
1 vs 2	3D	9.8	0.07	4.8
3 vs 4	3D	4.0	0.15	1.8

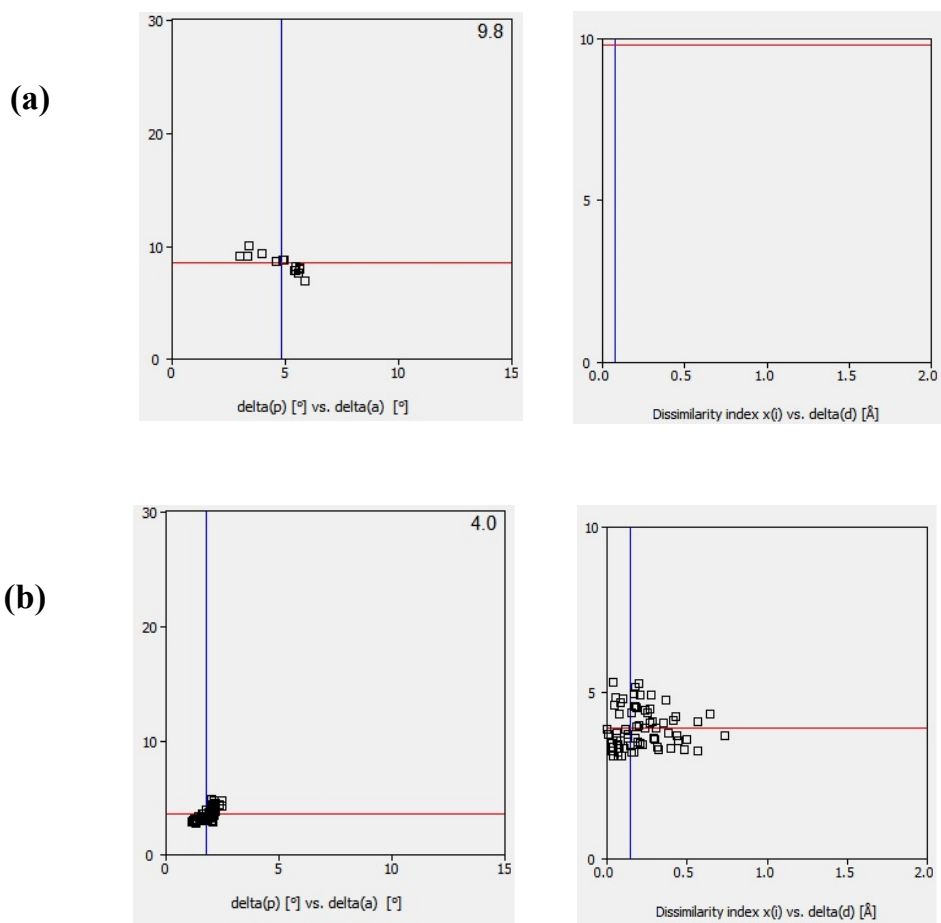


Figure S2 The plot of similarity index between structures of **1** and **3** with **2** (a) and **4** (b) respectively.

Table S4 Natural atomic orbital occupancies for NCS^- and Thiophene molecules from NBO analysis at B3LYP/6-311+G** level

NCS^-	Orbital Val(3p)	Occupancy
S_{NCS^-}	p_x	1.60
S_{NCS^-}	p_y	1.60
S_{NCS^-}	p_z	1.04
Thiophene		
S_{thio}	p_x	1.37
S_{thio}	p_y	0.93
S_{thio}	p_z	1.61

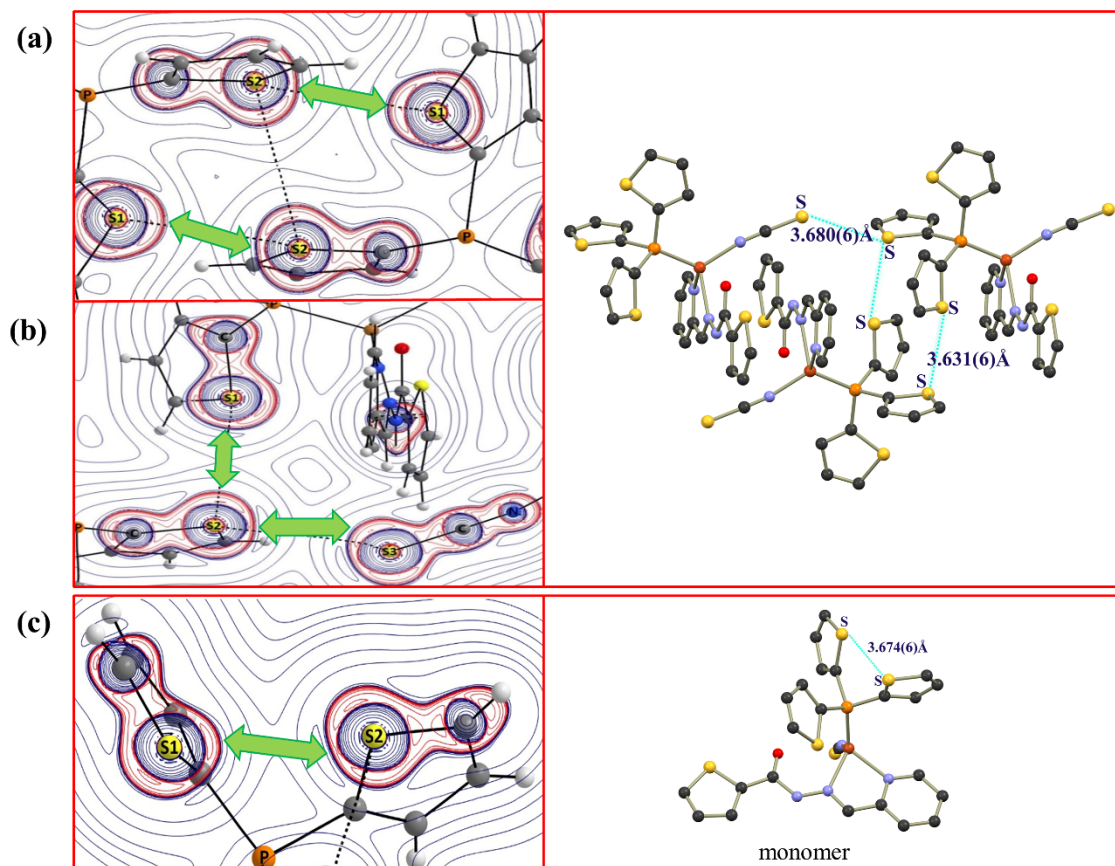


Figure S3 (a) and (b) Contour maps of the Laplacian of the electron density ($\nabla^2\rho$) for compounds **4**; (c) Contour maps of the Laplacian of the electron density ($\nabla^2\rho$) for compounds **4** monomer form. Red and blue lines correspond to the negative and positive values of $\nabla^2\rho$, respectively. Lump-hole interactions are shown by green arrows.

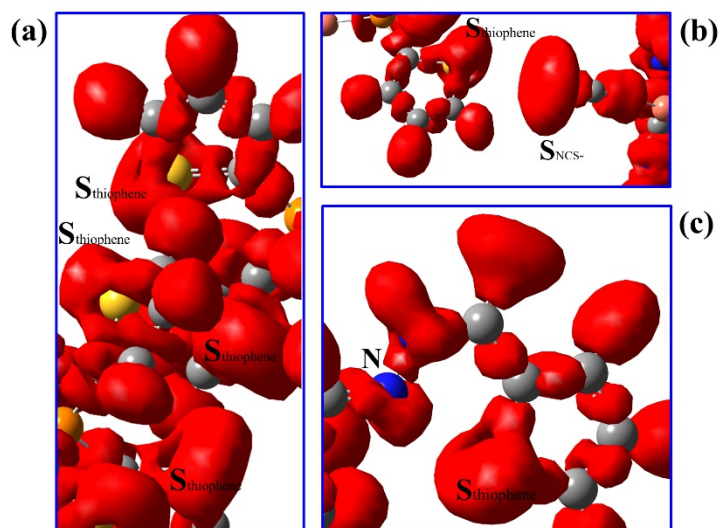


Figure S4 Elf map at 0.7 isosurface for **4** (a), (b) and **5** (c).

Computational details

For all calculations, the considered structures were taken directly from the CIF data. All DFT calculations and their electronic wave functions were computed using the Gaussian 09 suite of programs.³ Electronic density wave functions for AIM analysis were obtained at second order Coulomb-attenuating method (CAM) and hybrid functional methods of B3LYP with the 6-311++g** basis set. AIMAll program⁴ was used to calculate the Laplacian of the electron density. This package was also used to draw contour and relief maps of the Laplacian of the electron density. The electrostatic potentials map (ESP) has been calculated with Gaussian 09 facilities. The interaction energies have been corrected for the basis set superposition error (BSSE) using counterpoise procedure.⁵ The electron localization function (ELF)⁶ has been obtained with the Multiwfn program.⁷

Notes and references

1. G. M. Sheldrick, *Acta Cryst.*, 2015, C71, 3-8.
2. CrysAlis 171.38.43 package of programs, *Rigaku Oxford Diffraction*, 2015.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. *Gaussian 09*, revision D.01, Gaussian, Inc. Wallingford, CT, 2010.
4. T. A. Keith, *AIMAll (version 10.05.04)*, TK Gristmill Software, Overland Park, KS, 2010.
5. S. F. Boys and F. d. Bernardi, *Molecular Physics*, 1970, **19**, 553-566.
6. B. Silvi and A. Savin, *Nature*, 1994, **371**, 683.
7. T. Lu and F. Chen, *Journal of computational chemistry*, 2012, **33**, 580-592.