Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for the article

From single-point to three-point halogen bonding between zinc(II) tetrathiocyanate and tetrabromomethane.

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Table S1. Energies, ZPE and BSSE (in Hartrees) of the halogen-bonded complexes and their components.

	N	E	ZPE	BSSE
		ωB97XD, gas phase		
$Zn(NCS_4)^{2-}\cdot CBr_4$	3	-14078.733575	0.049112	0.001091
$Zn(NCS_4)^{2-}\cdot CBr_4$	2	-14078.732163	0.049156	0.000773
$NCS^-\cdot CBr_4$	1	-10825.955729	0.016304	0.000426
$Zn(NCS_4)^{2-}$	-	-3743.961454	0.041008	
CBr_4	-	-10334.762810	0.007184	
NCS^-	-	-491.187510	0.008770	
		M062X, gas phase		
$Zn(NCS_4)^{2-}\cdot CBr_4$	3	-14078.459958	0.049812	0.001194
$Zn(NCS_4)^{2-}\cdot CBr_4$	2	-14078.459652	0.049689	0.000814
$NCS^-\cdot CBr_4$	1	-10825.859835	0.016850	0.000531
$Zn(NCS_4)^{2-}$	-	-3743.696774	0.041786	
CBr_4	-	-10334.742253	0.007237	
NCS^-	-	-491.098064	0.008729	
		ωB97XD, dichloromethane		
$Zn(NCS_4)^{2-}\cdot CBr_4$	3	-14078.555092	0.049565	0.000783
$Zn(NCS_4)^{2-}\cdot CBr_4$	2	-14078.555030	0.049591	0.000783
$NCS^-\cdot CBr_4$	1	-10825.885100	0.016378	0.000531
$Zn(NCS_4)^{2-}$	-	-3743.775405	0.041717	
CBr_4	-	-10334.761269	0.007277	
NCS^-	-	-491.105591	0.008779	

Atomic coordinates of the calculated halogen-bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ complexes

Three-point bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ ωB97XD, gas phase

Br	1.85806700	-0.52302100	-1.75034500
Br	1.83389700	-1.22454200	1.33935800
Br	1.90075800	1.80284800	0.40302700
Br	4.48745500	-0.03610700	0.00530000
C	2.51178200	0.00505700	-0.00076200
Zn	-2.66330900	-0.01133700	0.00235200
S	-0.69663900	-1.30454800	-4.16757800
S	-7.45217300	0.02197400	-0.00630000
S	-0.71102200	4.25726600	0.96012300
S	-0.69428100	-2.96854500	3.20904200
N	-1.97907000	-0.57494700	-1.78127700
N	-4.64756700	0.00838800	-0.00093800
N	-1.95881700	1.80481900	0.41257300
N	-1.99269300	-1.28279400	1.38043200
C	-1.45403900	-0.88018300	-2.77832400
C	-5.81616500	0.01427900	-0.00332400
C	-1.44610800	2.82845900	0.64142800
C	-1.46114600	-1.98723600	2.14471300

Two-point bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ ωB97XD, gas phase

Zn	3.23470500	0.00007200	0.00029800
S	0.34493700	0.05181100	-3.83833900
S	0.34420400	-0.06305500	3.83865600
S	5.99142900	3.91325100	0.05649000
S	6.00633700	-3.90252400	-0.05651600
N	2.06438400	0.02089400	-1.61938200
N	2.06508100	-0.02614800	1.62087000
N	4.36205900	1.63148700	0.02434900
N	4.37005400	-1.62575600	-0.02282800
C	1.35548200	0.03398900	-2.54537800
C	1.35011700	-0.04333200	2.54193300
C	5.04129400	2.58265100	0.03773500
C	5.05223000	-2.57477100	-0.03710400
Br	-2.05682100	0.02225600	-1.58496500
Br	-2.05901800	-0.02518300	1.58610200
Br	-4.34120100	-1.58635700	-0.02455600
Br	-4.33697400	1.58958600	0.02292800
C	-3.17783100	0.00016300	-0.00010000

Three-point bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ M062X, gas phase

Br	1.78996300	-0.51883200	1.75576900
Br	1.78392800	1.77964500	-0.42648300
Br	1.78272900	-1.25941000	-1.32576500
Br	4.41164500	0.00155100	-0.00533200
C	2.43512200	0.00072500	-0.00040800
Zn	-2.61226500	-0.00072600	0.00013000
S	-0.56975700	-1.24274800	4.17405400
S	-7.42526800	0.00177400	0.00032400
S	-0.57243600	-2.99932400	-3.15905600
S	-0.57495500	4.23741700	-1.01191700
N	-1.91081100	-0.53961200	1.81191100
N	-4.62050700	-0.00051800	0.00116600
N	-1.91423300	-1.30127800	-1.37339900
N	-1.91279000	1.83840900	-0.43982100
C	-1.36542500	-0.83379100	2.80002300
C	-5.78812500	0.00027500	0.00075400
C	-1.36852200	-2.01161300	-2.12036000
C	-1.36876800	2.84198500	-0.67900400

Two-point bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ M062X, gas phase

Zn	-3.18006600	-0.00011400	-0.00001400
S	-0.28942800	0.39008200	3.85014600
S	-0.28942200	-0.39426100	-3.84977300
S	-5.96860500	3.90041100	-0.38729800
S	-5.97639600	-3.89514400	0.38684100
N	-1.99198600	0.16136600	1.62871000
N	-1.99196300	-0.16435300	-1.62844600
N	-4.32369500	1.64028200	-0.16273300
N	-4.32742700	-1.63795100	0.16241500
C	-1.29221300	0.25671600	2.55545700
C	-1.29218000	-0.26013900	-2.55514100
C	-5.00855100	2.58161200	-0.25613000
C	-5.01404600	-2.57799400	0.25582300
Br	2.01181900	0.16470700	1.57999500
Br	2.01181400	-0.16572700	-1.57986500
Br	4.29026800	-1.57781400	0.16553400
Br	4.28907400	1.57854400	-0.16560400
C	3.12781500	-0.00006300	0.00001500

Three-point bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ ωB97XD, CH_2Cl_2

Zn	-3.15104600	0.00003400	0.00009300
S	-0.43255800	3.81860400	0.98810500
S	-0.43257100	-3.81839500	-0.98849400
S	-5.91995900	0.99962000	-3.77489500
S	-5.92059100	-0.99971700	3.77456300
N	-2.00672400	1.57251200	0.41301800
N	-2.00668800	-1.57243100	-0.41278100
N	-4.30356700	0.41344100	-1.56324200
N	-4.30366600	-0.41339400	1.56333900
C	-1.35627200	2.51218100	0.65378400
C	-1.35627800	-2.51205600	-0.65383400
C	-4.97797000	0.65837100	-2.48633500
C	-4.97826100	-0.65839300	2.48627400
Br	2.03535300	1.53625200	0.39544700
Br	2.03538000	-1.53622500	-0.39577000
Br	4.29571700	-0.39625400	1.53856600
Br	4.29632900	0.39610800	-1.53804900
C	3.16370100	-0.00002800	0.00004400

Two-point bonded $Zn(NCS_4)^{2-}\cdot CBr_4$ ωB97XD, CH_2Cl_2

Zn	-3.15104600	0.00003400	0.00009300
S	-0.43255800	3.81860400	0.98810500
S	-0.43257100	-3.81839500	-0.98849400
S	-5.91995900	0.99962000	-3.77489500
S	-5.92059100	-0.99971700	3.77456300
N	-2.00672400	1.57251200	0.41301800
N	-2.00668800	-1.57243100	-0.41278100
N	-4.30356700	0.41344100	-1.56324200
N	-4.30366600	-0.41339400	1.56333900
C	-1.35627200	2.51218100	0.65378400
C	-1.35627800	-2.51205600	-0.65383400
C	-4.97797000	0.65837100	-2.48633500
C	-4.97826100	-0.65839300	2.48627400
Br	2.03535300	1.53625200	0.39544700
Br	2.03538000	-1.53622500	-0.39577000
Br	4.29571700	-0.39625400	1.53856600
Br	4.29632900	0.39610800	-1.53804900
C	3.16370100	-0.00002800	0.00004400

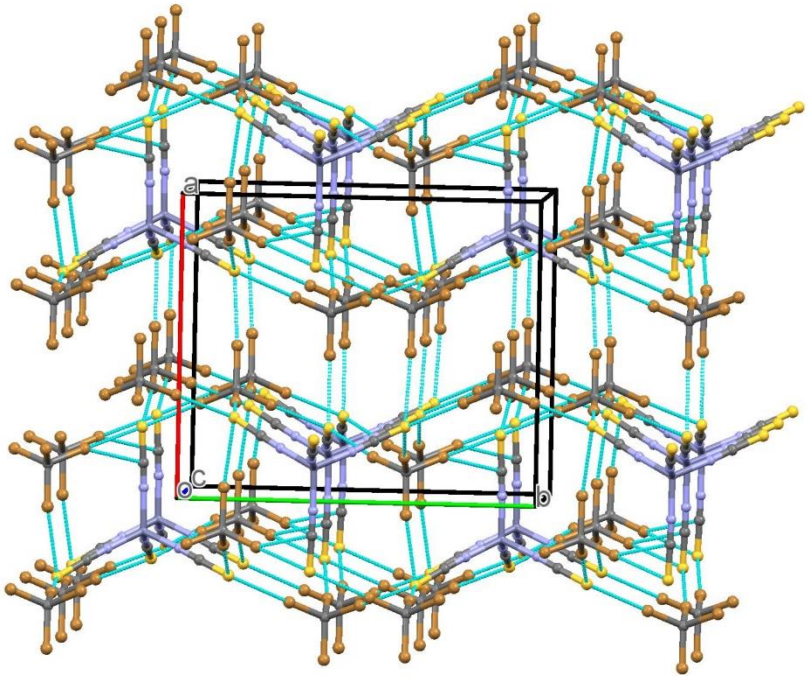

Figure S1. 3D-honeycomb network in the $(Bu_4N)_2[Zn(NCS)_4]\cdot 3CBr_4$ co-crystals(view nearly along c axes). Halogen bonds are shown as blue lines and Bu_4N^+ cations are omitted for clarity

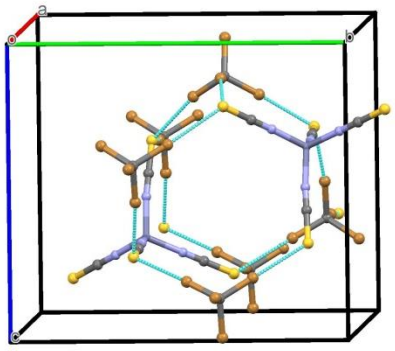

Figure S2. Fragment of the crystal structure of the $(Bu_4N)_2[Zn(NCS)_4]\cdot 3CBr_4$ co-crystals showing two types of rings formed by single-point and double-point halogen bonding.

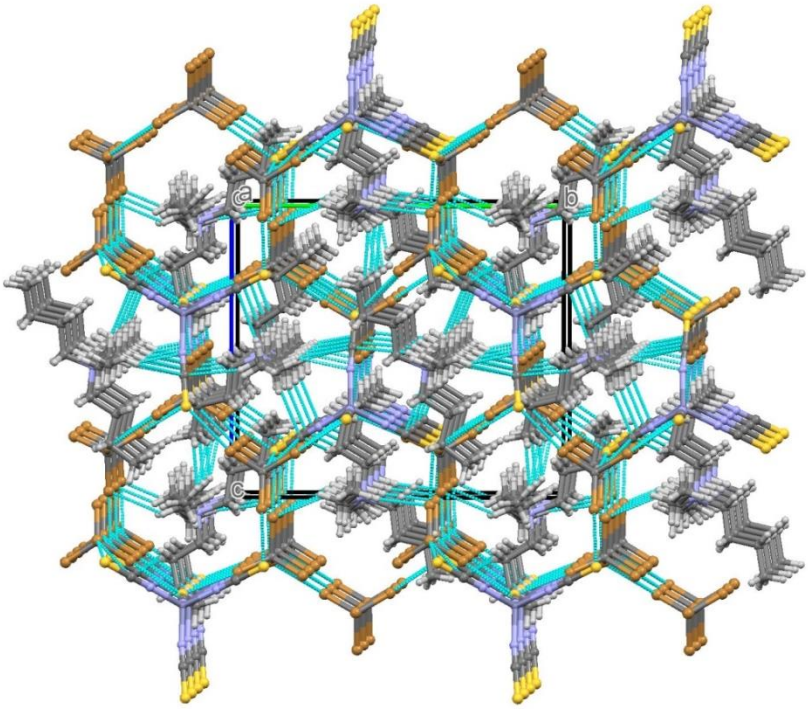

Figure S3. Honeycomb-like network in the $(Bu_4N)_2[Zn(NCS)_4]\cdot 3CBr_4$ co-crystals in which channels are filled with Bu_4N^+ counterions.

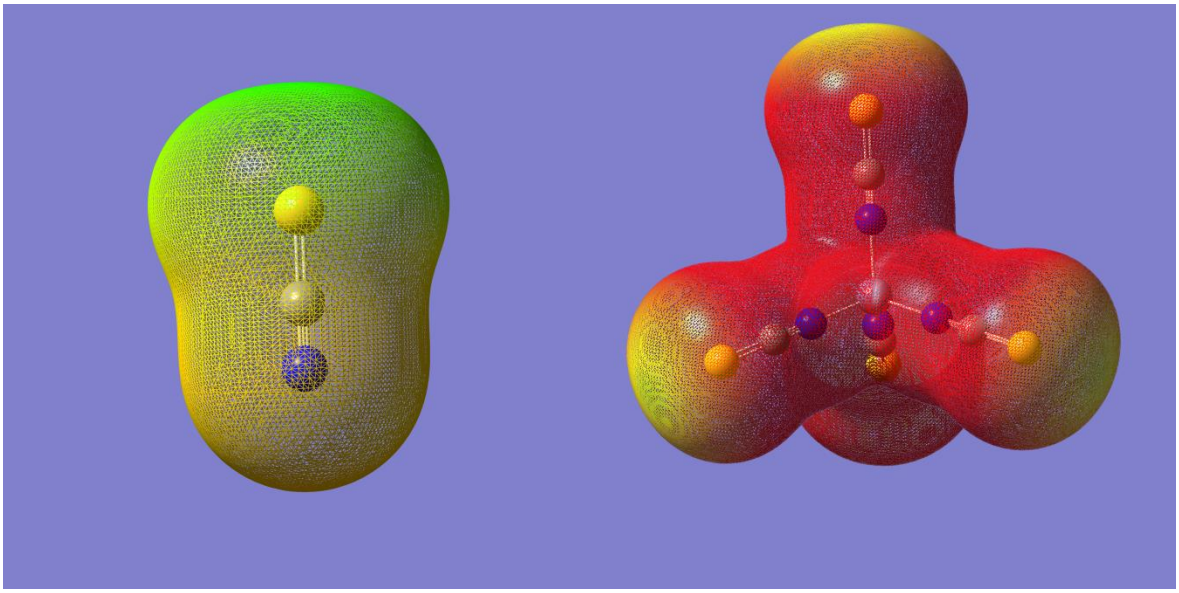

Figure S4. Surface electrostatic potential of NCS^- and $[Zn(NCS)_4]^{2-}$ calculated at calculated at isovalue 0.0004. ESP values: red: -110 to -120 kcal/mol, yellow-100 to -110 kca/mol, green: -90 top -100 kcal/mol.