

## Electronic Supplementary Information

# Electron Belt-to- $\sigma$ -Hole Switch of Noncovalently Bound Iodine(I) Atoms in Dithiocarbamate Metal Complexes

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## Experimental Section

**1. Materials and instrumentation.** Solvents were obtained from commercial sources and used as received. Et<sub>2</sub>NCS<sub>2</sub>Na trihydrate is commercially available and was recrystallized before use by adding Et<sub>2</sub>O to hot ethanol solution followed by refrigerator cooling ( $-10\text{ }^{\circ}\text{C}$ ) and filtration. Metal complexes **1–2** are commercially available and were purified by Soxhlet extraction followed by recrystallisation from CHCl<sub>3</sub>. Metal complexes **3–4** was synthesized accordingly to the modified published procedures:<sup>1, 2</sup> to a stirred solution of Et<sub>2</sub>NCS<sub>2</sub>Na trihydrate (100 mg, 0.443 mmol) in mixed solvent (EtOH:H<sub>2</sub>O 1:1, v/v; 7 mL) was added dropwise over a period of 3 min a solution of K<sub>2</sub>MCl<sub>4</sub> (0.220 mmol, M = Pd, Pt) in H<sub>2</sub>O (10 mL). Immediately formed precipitation was stirred for additional 20 min and then was filtered off with deionized H<sub>2</sub>O washing (3 x 15 mL). The precipitation was dried and stored over P<sub>4</sub>O<sub>10</sub>.

**2. Crystal growth.** Co-crystallization of **1–4** with FIB. A mixture of 0.250 mmol of any one of **1–4** and 0.504 mmol of FIB (25.7 mg) was dissolved in dichloromethane (2.5 mL), whereupon the formed solution was left to stand at room temperature for slow evaporation. Crystals of **(1–4)·2FIB** suitable for X-ray diffraction analysis were obtained after 2–5 d.

**3. X-ray structure determinations.** The X-ray diffraction experiments were carried out on the Rigaku “XtaLAB SuperNova” diffractometer using monochromated CuK $\alpha$  radiation. The crystals were thermostated at 100 K at all experiments. The structures were solved within Olex2<sup>3</sup> GUI package by the ShelXT<sup>4</sup> using Intrinsic Phasing method and refined by the ShelXL<sup>5</sup> refinement package using least square minimization. Since the betta parameter for all structures is close to the 90° edge, in order to maintain uniformity, the unit cell parameters of the platinum and palladium dithiocarbamates were converted to an unreduced cell using WinGX<sup>6</sup> program. Empirical absorption correction was applied in CrysAlisPro (Rigaku Oxford Diffraction, 2019) program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Supplementary crystallographic data for this paper have been deposited at Cambridge

Crystallographic Data Centre (CCDC 2044963–2044966) and can be obtained free of charge via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

**4. Details of Hirshfeld surface analysis.** The Hirshfeld surface analysis was carried out using the CrystalExplorer program.<sup>7-10</sup> The contact distances ( $d_{\text{norm}}$ ), based on  $R_{\text{vdW}}$ ,<sup>11</sup> were mapped on the Hirshfeld surfaces. In the color scale, the negative values of  $d_{\text{norm}}$  were visualized by red color indicating the contacts shorter than  $\Sigma_{\text{vdW}}$ . The values represented in white color denote the intermolecular distances close to the contacts with  $d_{\text{norm}}$  equal to zero. The contacts longer than  $\Sigma_{\text{vdW}}$  with positive  $d_{\text{norm}}$  values were colored with blue.

**5. Computational details.** The calculations of the dimers shown in **Figures 8–9** were performed at the DFT level of theory using PBE0 functional,<sup>12</sup> the def2-TZVP basis set<sup>13</sup> and the D3 dispersion correction<sup>14</sup> with the help of the Turbomole 7.0 program package.<sup>15</sup> The topological analysis of the electron density distribution has been analyzed with the help of the atoms in molecules (QTAIM) method developed by Bader<sup>16</sup> as well as noncovalent interaction plot (NCIPlot)<sup>17, 18</sup> by using the AIMAll program.<sup>19</sup> The estimation of the individual XB energies was carried out using the QTAIM method and the V(r) predictor as recently proposed in the literature.<sup>20</sup> The electron localization function (ELF) projections along the planes as well as ELF, electron density, and electrostatic potential (calculated with LIBRETA<sup>21</sup>) projections along the bond paths were plotted in Multiwfn 3.8.<sup>22</sup> The MEP surfaces and NBO analysis<sup>23</sup> were computed at the PBE0-D3/def2-TZVP level of theory by means of the Gaussian-16 program.<sup>24</sup> The MEP plots of **Figures S1–S2** were represented using the 0.001 a.u. isosurface.

## Applications of dithiocarbamates

The homoleptic dithiocarbamates [ $M(S_2CNR_2)_2$ ] (**Figure 2**; R = Et) found their applications in medicine,<sup>25-45</sup> photovoltaics,<sup>46-48</sup> syntheses of metal sulfides<sup>39, 48-56</sup> and polinuclear coordination compounds;<sup>57-78</sup> these metal complexes are useful as luminescent materials<sup>42-45, 79-81</sup> and chemical sensors.<sup>42, 48, 50, 82, 83</sup>

# Crystallographic data

**Table S1.** Crystallographic data and structure refinement for (**1–4**)·2FIB.

Identification code	<b>1</b> ·2FIB	<b>2</b> ·2FIB	<b>3</b> ·2FIB	<b>4</b> ·2FIB
CCDC number	2044963	2044964	2044966	2044965
Empirical formula	C <sub>22</sub> H <sub>20</sub> CuF <sub>6</sub> I <sub>6</sub> N <sub>2</sub> S <sub>4</sub>	C <sub>22</sub> H <sub>20</sub> F <sub>6</sub> I <sub>6</sub> N <sub>2</sub> NiS <sub>4</sub>	C <sub>22</sub> H <sub>20</sub> F <sub>6</sub> I <sub>6</sub> N <sub>2</sub> PdS <sub>4</sub>	C <sub>22</sub> H <sub>20</sub> F <sub>6</sub> I <sub>6</sub> N <sub>2</sub> PtS <sub>4</sub>
Formula weight	1379.58	1374.75	1422.44	1511.13
Temperature, K		100(2)		
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a, Å	8.6789(3)	8.6870(2)	8.6378(2)	8.6611(2)
b, Å	9.4436(3)	9.4313(2)	9.5068(3)	9.6024(2)
c, Å	12.4868(2)	12.2577(2)	12.3335(3)	12.1690(2)
α, °	107.682(2)	106.930(2)	107.763(3)	107.288(2)
β, °	90.978(2)	91.1590(10)	89.773(2)	89.909(2)
γ, °	114.817(3)	113.553(2)	113.626(3)	113.544(2)
Volume, Å <sup>3</sup>	872.57(5)	869.96(3)	875.50(5)	877.93(3)
Z	1	1	1	1
ρ <sub>calc</sub> , g·cm <sup>-3</sup>	2.625	2.624	2.698	2.858
μ, mm <sup>-1</sup>	45.254	45.309	48.499	51.576
F(000)	631.0	630.0	648.0	680.0
Crystal size, mm <sup>3</sup>	0.17 × 0.15 × 0.14	0.2 × 0.18 × 0.15	0.15 × 0.14 × 0.12	0.20 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54184)			
2Θ range for data collection, °	7.536 to 134.96	7.632 to 124.91	7.596 to 140.984	7.678 to 140.876
Index ranges	−10 ≤ h ≤ 10, −11 ≤ k ≤ 11, −14 ≤ l ≤ 14	−9 ≤ h ≤ 9, −10 ≤ k ≤ 10, −14 ≤ l ≤ 13	−10 ≤ h ≤ 10, −11 ≤ k ≤ 11, −15 ≤ l ≤ 15	−10 ≤ h ≤ 10, −11 ≤ k ≤ 11, −14 ≤ l ≤ 14
Reflections collected	14534	14447	16237	7998
Independent reflections	3146 [R <sub>int</sub> = 0.0581, R <sub>sigma</sub> = 0.0386]	2765 [R <sub>int</sub> = 0.0537, R <sub>sigma</sub> = 0.0261]	3340 [R <sub>int</sub> = 0.0499, R <sub>sigma</sub> = 0.0352]	3352 [R <sub>int</sub> = 0.0448, R <sub>sigma</sub> = 0.0529]
Data/restraints/parameters	3146/0/189	2765/0/189	3340/0/189	3352/0/183
Goodness-of-fit on F <sup>2</sup>	1.032	1.096	1.072	1.011
Final R indexes [I ≥ 2σ(I)]	R <sub>1</sub> = 0.0346, wR <sub>2</sub> = 0.0882	R <sub>1</sub> = 0.0366, wR <sub>2</sub> = 0.0985	R <sub>1</sub> = 0.0352, wR <sub>2</sub> = 0.0916	R <sub>1</sub> = 0.0348, wR <sub>2</sub> = 0.0842
Final R indexes [all data]	R <sub>1</sub> = 0.0386, wR <sub>2</sub> = 0.0899	R <sub>1</sub> = 0.0371, wR <sub>2</sub> = 0.0990	R <sub>1</sub> = 0.0383, wR <sub>2</sub> = 0.0941	R <sub>1</sub> = 0.0381, wR <sub>2</sub> = 0.0871
Largest diff. peak/hole, e·Å <sup>-3</sup>	2.41/−1.00	1.73/−2.57	1.27/−2.17	1.70/−1.86

**Table S2.** Geometrical parameters of the chelated S1C1S2 rings in the metal complexes in their co-crystals.

M	Cu	Ni	Pd	Pt
$d(M1-S1)$ , Å	2.2988(12)	2.2066(14)	2.3280(13)	2.3276(14)
$d(M1-S2)$ , Å	2.3164(13)	2.2131(14)	2.3325(13)	2.3270(15)
$d(S1-C1)$ , Å	1.732(5)	1.729(6)	1.741(6)	1.718(6)
$d(S2-C1)$ , Å	1.720(5)	1.723(6)	1.738(6)	1.739(6)
$\angle(S1-C1-S2)$ , °	113.4(3)	109.4(3)	110.0(3)	110.1(3)
$\angle(S1-M1-S2)$ , °	77.36(4)	79.22(5)	75.35(5)	74.99(5)
$\angle(M1-S1-C1)$ , °	84.74(16)	85.7(2)	87.4(2)	87.7(2)
$\angle(M1-S2-C1)$ , °	84.46(18)	85.6(2)	87.3(2)	87.7(2)

## Results of Hirshfeld surface analysis

**Table S3.** Results of Hirshfeld surface analysis for the X-ray diffraction structures of the co-crystals.

Structure	Contributions of different intermolecular contacts to the molecular Hirshfeld surface*
<b>1·2FIB</b>	I···Cu 2.9%, I···S 8.6%, I···C 1.2%, I···H 12.8%, S···H 23.4%, F···H 21.1%, N···H 1.0%, C···H 10.0%, H···H 18.0%
<b>2·2FIB</b>	I···Ni 2.9%, I···S 9.1%, I···C 1.0%, I···H 13.6%, S···H 21.8%, F···H 22.0%, N···H 1.0%, C···H 9.9%, H···H 17.8%
<b>3·2FIB</b>	I···Pd 3.1%, I···S 8.6%, I···H 13.7%, S···H 23.2%, F···H 22.3%, C···H 9.5%, H···H 16.5%
<b>4·2FIB</b>	I···Pt 3.3%, I···S 9.0%, I···H 14.2%, S···H 22.6%, F···H 22.5%, C···H 9.5%, H···H 15.8%

\*The contributions of all other intermolecular contacts do not exceed 1%.

## Noncovalent interactions

**Table S4.** Parameters of the C–I…S and C–I…M/M…I–C short contacts in the co-crystals.

Parameter	1·2FIB	2·2FIB	3·2FIB	4·2FIB
$d(I1S\cdots M1)$ , Å	3.3924(3)	3.3388(4)	3.3732(4)	3.3351(4)
$R_{\text{Bondi}}$	1.00	0.92	0.93	0.89
$\angle(C1S-I1S\cdots M1)$ , °	137.06(16)	149.1(2)	153.0(2)	160.1(2)
$d(I1S\cdots S1)$ , Å	3.4523(11)	3.6826(13)	3.8447(12)	4.0172(14)
$R_{\text{Bondi}}$	0.91	0.97	1.02	1.06
$\angle(C1S-I1S\cdots S1)$ , °	175.89(18)	174.15(19)	169.18(19)	164.0(2)
$d(I1S\cdots S2)$ , Å	3.8775(13)	3.7383(15)	3.7221(14)	3.6931(16)
$R_{\text{Bondi}}$	1.03	0.99	0.98	0.98
$\angle(C1S-I1S\cdots S2)$ , °	133.30(15)	140.2(2)	143.7(2)	145.4(2)
$d(I2S\cdots S2)$ , Å	3.3994(12)	3.4089(15)	3.3929(13)	3.4161(15)
$R_{\text{Bondi}}$	0.90	0.90	0.90	0.90
$\angle(C3S-I2S\cdots S2)$ , °	169.01(13)	166.25(17)	165.12(14)	163.87(16)

<sup>a</sup>  $R_{\text{Bondi}}^{84} = d/\Sigma_{\text{vdW}}$ ;  $\Sigma_{\text{vdW}}(\text{I, Cu}) = 3.38$  Å,  $\Sigma_{\text{vdW}}(\text{I, Ni}) = 3.61$  Å,  $\Sigma_{\text{vdW}}(\text{I, Pd}) = 3.61$  Å,  $\Sigma_{\text{vdW}}(\text{I, Pt}) = 3.73$  Å,  $\Sigma_{\text{vdW}}(\text{I, S}) = 3.78$  Å.

**Table S5.** Previously reported R–I…M (M = Ni, Pd, Pt) halogen bonding.

Structure	$d(\text{I}\cdots\text{M})$ , Å	$R_{IM}$	$\angle(R-\text{I}\cdots\text{M})$ , °	Refs.
<b>M = Ni</b>				
2·2FIB	3.3388(4)	0.92	149.1(2)	<i>This work</i>
AMIJAJ	3.4702(17)	0.96	177.8(4)	<sup>85, 86</sup>
<b>M = Pd</b>				
LOFXAH	3.0953(6)	0.86	178.871(12)	<sup>87</sup>
	3.1021(6)	0.86	178.192(11)	
3·2FIB	3.3732(4)	0.93	153.0(2)	<i>This work</i>
AMIJIR	3.4978(3)	0.97	177.57(7)	<sup>85, 88</sup>
LIHMEX	3.5125(4)	0.97	164.94(15)	<sup>88</sup>
IJIFEP	3.5433(4)	0.98	170.61(9)	<sup>89</sup>
IJIDUD	3.6422(4)	1.01	167.68(13)	<sup>89</sup>
<b>M = Pt</b>				
PIDRIE	2.8198(3)	0.76	177.533(15)	<sup>90</sup>
	2.8260(3)	0.76	177.248(14)	
DUGJUK	2.895(1)	0.78	179.42(4)	<sup>91</sup>
DEJHEF	2.906(2)	0.78	176.91(4)	<sup>91</sup>
	2.968(2)	0.80	177.72(6)	<sup>92</sup>
XUVXUK	3.0891(4)	0.83	167.8(2)	<sup>93</sup>
	3.0979(4)	0.83	177.60(17)	
	3.1264(4)	0.84	175.99(18)	
	3.1379(4)	0.84	167.5(2)	

XUVXOE	3.1933(3)	0.86	174.11(10)	<sup>93</sup>
XUVYAR	3.2494(4)	0.87	174.28(16)	<sup>93</sup>
<b>4·2FIB</b>	<b>3.3351(4)</b>	<b>0.89</b>	<b>160.1(2)</b>	<i>This work</i>
UKELAZ	3.4023(5)	0.91	172.7(2)	<sup>94</sup>
UKEKOM	3.4276(5)	0.92	164.80(17)	<sup>94</sup>
UKEKIG	3.4389(5)	0.92	169.8(3)	<sup>94</sup>
ROZZUE	3.4504(3)	0.93	168.75(10)	<sup>95</sup>
AMIJEN	3.4666(4)	0.93	177.14(13)	<sup>85, 88</sup>
XUVYEV	3.4743(8)	0.93	168.6(2)	<sup>93</sup>
UKAWOU	3.7060(7)	0.99	158.4(2)	<sup>94</sup>

*Comments to semicoordinative/XB I···(S–Cu) contact (section 2.2.1).* Complexes [Cu<sup>II</sup>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>] are known<sup>96–98</sup> as weak Cu-centered electrophiles, which according to the EPR data can coordinate two pyridines.<sup>96</sup> These metal complexes tend to dimerize or polymerize through a pair of Cu<sup>II</sup>···S semicoordinative interactions (**Figure 6J**).<sup>28, 67, 99–102</sup> We assume that these data, together with performed theoretical calculations (**section 3**) confirm the semicoordinative nature of the Cu<sup>II</sup>···I–C contact in the structure of **1·2FIB** even considering that  $\angle(\text{Cu}^{\text{II}}\cdots\text{I–C})$  137.06(16) $^\circ$  is substantially larger than 90 $^\circ$ .

The nucleophilic nature of the I1S atom in the Cu1···I1S–C1S contact is not unprecedented. Similar interaction of iodine atom via its electron belt has been observed in CSD structure OJIJC, where type II iodine···iodine contact C43–I5···I2–C33 between FIBs was identified. In OJIJC structure, the angle around the nucleophilic I2 atom (135.83(8) $^\circ$ ) is close to  $\angle(\text{Cu}^{\text{II}}\cdots\text{I–C})$  137.06(16) $^\circ$ , which we observed in the structure of **1·2FIB**. This comparison provides certain evidences favoring the nucleophilic role of FIB toward the copper(II) center.

*Comments to the C–I···Ni halogen bonding (section 2.2.2).* Our observation of nickel(II)-involving XB correlates with the previously reported C–H···Ni<sup>II</sup> hydrogen bonding in the structures of various nickel(II) dithiocarbamates (**Figure 7L**).<sup>47, 103–109</sup>

*Comments to the C–I···Pd halogen bonding (section 2.2.3.).* Similar to the nickel(II) center in the structure of **2·2FIB**, the palladium(II) atom in **3·2FIB** can also form both Pd<sup>II</sup>···I semicoordination bond and I···Pd<sup>II</sup> XB (**Table 4**). The structure of [Pd( $\mu$ -SCH<sub>2</sub>CO<sub>2</sub>Me)<sub>2</sub>]<sub>8</sub>·I<sub>2</sub><sup>87</sup>

(LOFXAH) demonstrates the shortest I···Pd<sup>II</sup> XB (3.0953(6) Å and 3.1021(6) Å) and the formation of the strong XB is accounted for by the deep σ<sub>h</sub> of I<sub>2</sub> and the inclusion character of the co-crystal. The longest I···Pd<sup>II</sup> XB has been reported for *trans*-[PdCl<sub>2</sub>(NCNMe<sub>2</sub>)<sub>2</sub>]·2CHI<sub>3</sub> (3.5125(4) Å) (LIHMEX).<sup>88</sup> A slightly shorter I···Pd<sup>II</sup> XB can be found in [Fe(2-iodopyrazine)(H<sub>2</sub>O)M<sup>II</sup>(CN)<sub>4</sub>] (M = Pd) MOF (3.4978(3) Å) (AMIJIR).<sup>85</sup> In a recent study by one of us,<sup>89</sup> the half-lantern complexes *trans*-(E,N)-[Pd(ppz)(μ-E<sup>◦</sup>N)]<sub>2</sub> (E<sup>◦</sup>N is a deprotonated 2-substituted pyridine; E = S, Se; Hppz = 1-phenylpyrazole) were cocrystallized with 1,4-diiidotetrafluorobenzene to give *trans*-(E,N)-[Pd(ppz)(μ-E<sup>◦</sup>N)]<sub>2</sub>·2(1,4-diiidotetrafluorobenzene) (IJIFEP and IJIDUD). These two co-crystals are built by the joint action of I···Pd (3.6422(4) Å, E = S; 3.5433(4) Å, E = Se) and I···E XBs, thus furnishing clusters bearing the Pd<sup>II</sup><sub>2</sub>···I(arene<sup>F</sup>)I···E[@Pd<sup>II</sup><sub>2</sub>] linkages.

Notably, MOF is isostructural with previously mentioned nickel(II)-containing analog. Again, in **3**·2FIB, the C–I···Pd metal-involving XB (3.3732(4) Å) is shorter than in this MOF as well as in *trans*-[PdCl<sub>2</sub>(NCNMe<sub>2</sub>)<sub>2</sub>]·2CHI<sub>3</sub>, which confirms the increased nucleophilicity of metal center in the dithiocarbamate complex.

*Comments to the C–I···Pt halogen bonding (section 2.2.4).* Van Koten et al.<sup>90-92, 110</sup> reported the platinum(II) complex-diiodine adducts exhibiting short I–I···Pt<sup>II</sup> XB distances (2.8198(3)–2.968(2) Å; PIDRIE, DUGJUK, and DEJHEF; **Table 4**); this XB is so strong that it can be treated as coordinative XB.<sup>111</sup> The next strong contacts were observed in the co-crystals of the half-lantern complexes [{Pt(C<sup>◦</sup>N)(μ-S<sup>◦</sup>N)}<sub>2</sub>] (C<sup>◦</sup>N cyclometalated 2-Ph-benzothiazole; S<sup>◦</sup>N 2-SH-substituted N-heterocycles) with 1,4-diiidotetrafluorobenzene and 1,1'-I<sub>2</sub>-C<sub>6</sub>F<sub>4</sub>-C<sub>6</sub>F<sub>4</sub> (XUVXUK, XUVXOE, and XUVYAR), where metal centers exhibit an increased nucleophilicity toward XB donor.<sup>93</sup> Much weaker C–I···Pt<sup>II</sup> XB were identified by us<sup>94</sup> in *trans*-[PtCl<sub>2</sub>(NCNMe<sub>2</sub>)<sub>2</sub>]·2CHI<sub>3</sub> (UKEKIG, 3.4389(5) Å), *trans*-[PtCl<sub>2</sub>(NCNMe<sub>2</sub>)<sub>2</sub>]·0.5CHCl<sub>3</sub>·1.5CHI<sub>3</sub> (UKEKOM, 3.4276(5) Å), *trans*-[PtBr<sub>2</sub>(NCNMe<sub>2</sub>)<sub>2</sub>]·2CHI<sub>3</sub> (UKELAZ, 3.4023(5) Å), and the weakest one in *trans*-[PtCl<sub>2</sub>(NCN(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>]·2CHI<sub>3</sub> (UKAWOU, 3.7060(7) Å) as a part of the

three-center bifurcated C–I···(Cl–Pt<sup>II</sup>) XB. The third example of [Fe(2-iodopyrazine)(H<sub>2</sub>O)M<sup>II</sup>(CN)<sub>4</sub>] MOF (AMIJEN),<sup>85</sup> where M = Pt, is also isostructural with the Ni and Pd analogs and demonstrates the same C–I···Pt<sup>II</sup> XB (3.4666(4) Å). FIB is also known<sup>95</sup> to form the C–I···Pt<sup>II</sup> XB in the co-crystal [Pt(acac)<sub>2</sub>]·2FIB (3.4077(3) Å).

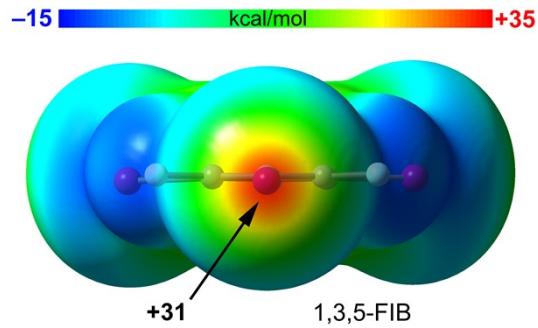
## Parameters of halogen bonds involving dithiocarbamate ligands

**Table S6.** Parameters of NM–X···S (NM – any nonmetal; X = Cl, Br, I) XBs with dithiocarbamate ligands found in CCDC literature data.  $d(X\cdots S)$  distances are fixed as less than  $\Sigma_{vdW}$ , and  $\angle(NM-X\cdots S)$  are set between 150 and 180 degrees. Only non-disordered moieties, structures with R ≤ 10% are under consideration.

Structure	M	NM–X···S	$d(X\cdots S)$ , Å	$R_{XS}^*$	$\angle(NM-X\cdots S), ^\circ$
<b>X = Cl</b>					
BOMCEM	Sn <sup>IV</sup>	C31–Cl1···S3	3.516(2)	0.99	167.9(3)
BOSHAV	Nd <sup>III</sup>	C14–Cl2···S1	3.302(4)	0.93	167.6(3)
BOSHID	Eu <sup>III</sup>	C14–Cl1···S3	3.302(4)	0.93	169.0(3)
BOSHOJ	Eu <sup>III</sup>	C20–Cl2···S1	3.5276(14)	0.99	158.81(16)
DIFQIU	Pd <sup>II</sup>	C125–Cl7···S3	3.415(3)	0.96	167.8(4)
DUBBEJ	Ag <sup>I</sup>	C41–Cl1···S2	3.5362(17)	1.00	162.41(18)
DUHNUQ	Zn <sup>II</sup>	C33–Cl3···S2	3.3864(15)	0.95	159.53(13)
EJIXAW	Ni <sup>II</sup>	C23–Cl3···S2	3.352(2)	0.94	169.0(3)
GUVQOD	Zn <sup>II</sup>	C71–Cl5···S8	3.4580(16)	0.97	162.69(16)
HOWHOQ	Zn <sup>II</sup>	C9–Cl2···S1	3.317(3)	0.93	155.7(3)
	Zn <sup>II</sup>	C9–Cl3···S1	3.335(3)	0.94	168.1(3)
JOVQIX	Sn <sup>IV</sup>	C20–Cl2···S2	3.313(3)	0.93	167.9(3)
KENYOT	Pd <sup>II</sup>	C35–Cl1···S5	3.361(3)	0.95	175.3(4)
KIHZOS	Zn <sup>II</sup>	C1–Cl2···S1	3.475(4)	0.98	150.9(5)
KOXLER	Nd <sup>III</sup>	C40–Cl1···S5	3.381(5)	0.95	162.8(5)
MECBCR	Cr <sup>III</sup>	C20–Cl6···S1	3.514(2)	0.99	172.819(9)
MIKWAF	Sb <sup>III</sup>	C28–Cl2···S3	3.4954(14)	0.98	179.05(17)
MORTMN	Mn <sup>III</sup>	C16–Cl1···S2	3.382(3)	0.95	153.36(3)
MOWSIC	Au <sup>III</sup>	C41–Cl10···S6	3.547(6)	1.00	164.1(8)
MTCTAC10	Ta <sup>V</sup>	C7–Cl2···S4	3.5393(12)	1.00	166.758(6)
NAMFUF	Zn <sup>II</sup>	C14–Cl2···S4	3.4425(16)	0.97	158.89(14)
NICFAI	Sm <sup>III</sup>	C34–Cl3···S4	3.5143(11)	0.99	178.50(8)
NICFEM	Nd <sup>III</sup>	C34–Cl2···S6	3.5121(12)	0.99	178.66(11)
OCOWAG	Ru <sup>III</sup>	C16–Cl1···S3	3.5139(17)	0.99	157.16(16)
OCURUC	Bi <sup>III</sup>	C38–Cl6···S11	3.2868(18)	0.93	155.63(18)
OXIXEA	Zn <sup>II</sup>	C29–Cl1···S5	3.245(5)	0.91	172.8(6)
	Zn <sup>II</sup>	C30–Cl5···S1	3.297(5)	0.93	173.8(6)
OZEGAD	Cu <sup>I</sup>	C42–Cl3···S1	3.3488(10)	0.94	161.93(11)
PAZTMP10	Mo <sup>VI</sup>	C17–Cl4···S3	3.5378(9)	1.00	162.590(6)
QEWPPO	Os <sup>II</sup>	C24–Cl3···S1	3.1643(16)	0.89	150.0(3)
SURBOZ	Cu <sup>I</sup>	C54–Cl1···S2	3.5027(13)	0.99	161.00(14)
VIXRUQ	Au <sup>I</sup>	C15–Cl1···S1	3.515(5)	0.99	163.8(6)
XOCGED	Cu <sup>II</sup>	C11–Cl1···S2	3.443(8)	0.97	151.5(9)
XOLFIN	Mo <sup>IV</sup>	C36–Cl9···S5	3.498(4)	0.99	158.2(3)
XONHIS	Sn <sup>IV</sup>	C25–Cl1···S2	3.374(2)	0.95	168.2(2)
YERHOV	Cu <sup>II</sup>	C10–Cl2···S1	3.4364(11)	0.97	150.17(13)
ZUHGIU	La <sup>III</sup>	C31–Cl3···S6	3.4802(12)	0.98	160.06(13)
<b>X = Br</b>					
KUCBAL	V <sup>IV</sup>	C11–Br1···S3	3.530(6)	0.97	166.4(6)
MANTEA	Ru <sup>II</sup>	C4–Br1···S2	3.4064(19)	0.93	166.9(2)
NOQWEX	Sn <sup>IV</sup>	C18–Br2···S1	3.619(3)	0.99	152.69(14)
VOXQEN	Cu <sup>II</sup>	C6–Br1···S1	3.556(3)	0.97	174.2(3)
<b>X = I</b>					
ETCBFE	Fe <sup>IV</sup>	I2–I1···S6	3.628(3)	0.96	178.3553(17)
IATCNI	Ni <sup>II</sup>	As1–I1···S2	3.7551(4)	0.99	164.101(3)
MUJBIC	Co <sup>III</sup>	I2–I2···S2	3.1441(8)	0.83	175.42(2)
	Co <sup>III</sup>	I1–I1···S3	3.1484(9)	0.83	175.706(15)
ROHXAN	Ru <sup>II</sup>	I1–I1···S2	3.177(2)	0.84	172.34(5)

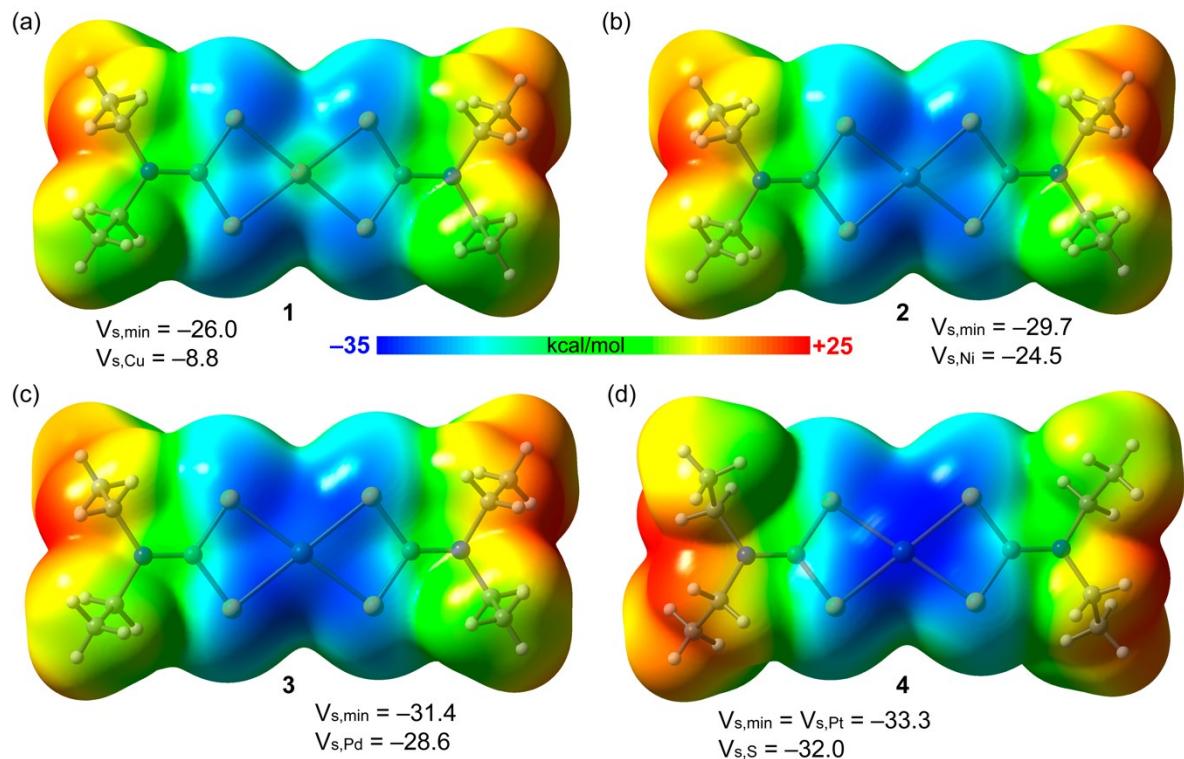
VIQFEH	Co <sup>III</sup>	I1–I1···S6	3.2281(12)	0.85	178.77(3)
${}^*R_{XS} = d(X \cdots S) / (R_{vdW}(X) + R_{vdW}(S))$					

## Theoretical studies

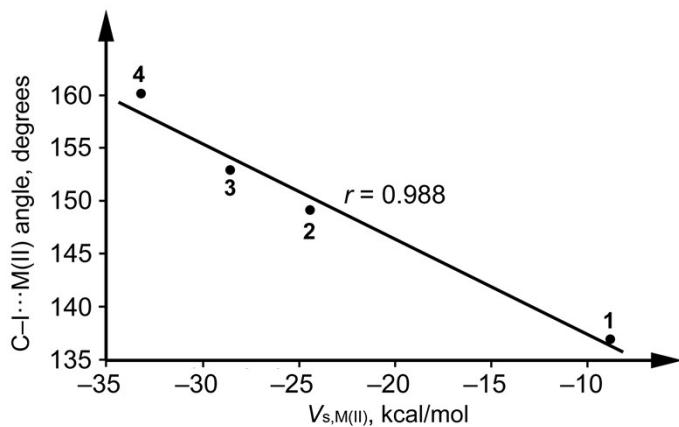


**Figure S1.** MEP surface (0.001 isosurface) of FIB at the PBE0-D3/def2-TZVP level of theory.

Energies in kcal/mol.



**Figure S2.** MEP surfaces (0.001 isosurface) of **1** (a), **2** (b), **3** (c), and **4** (d) at the PBE0-D3/def2-TZVP level of theory. Energies at S and M<sup>II</sup> centers are given in kcal/mol.



**Figure S3.** Regression plot of the C–I…M<sup>II</sup> angle of the XB interaction vs. the MEP value at the metal center ( $V_{s,M}^{II}$ ).

**Table S7.** QTAIM parameters ( $\rho$ ,  $\nabla^2\rho(r)$  and  $V(r)$  in a.u.) at the bond CP of I…S XB and I…H hydrogen bonds in the four model clusters reported herein (interactions depicted in **Figure 8**). Energy associated to each interaction based on the  $V_r$  parameter is also indicated (see computational methods)

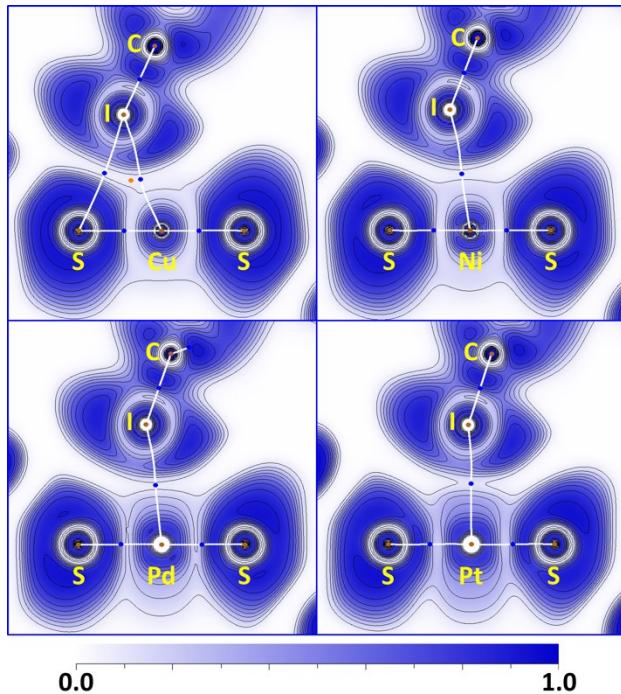
Model cluster	CP	$\rho(r)$	$\nabla^2\rho(r)$	$V(r)$	E
<b>1·FIB</b>	I…S	0.0138	0.0348	-0.0068	3.32
	H…I	0.0057	0.0153	-0.0025	0.78
<b>2·FIB</b>	I…S	0.0139	0.0342	-0.0068	3.32
	H…I	0.0060	0.0155	-0.0026	0.82
<b>3·FIB</b>	I…S	0.0139	0.0338	-0.0068	3.32
	H…I	0.0059	0.0155	-0.0026	0.82
<b>4·FIB</b>	I…S	0.0144	0.0350	-0.0071	3.47
	H…I	0.0060	0.0159	-0.0027	0.85

**Table S8.** QTAIM parameters ( $\rho$ ,  $\nabla^2\rho(r)$  and  $V(r)$  in a.u.) at the bond CP of I…S XB and I…M XBs or semicoordination in the four model clusters reported herein (interactions depicted in **Figure 9**). Energy associated to each interaction based on the  $V_r$  parameter is also indicated (see computational methods)

Model cluster	CP	$\rho(r)$	$\nabla^2\rho(r)$	$V(r)$	E
<b>1·FIB</b>	I…S	0.0132	0.0342	-0.0066	3.22
	I…Cu	0.0118	0.0238	-0.0068	3.32
<b>2·FIB</b>	I…Ni	0.0133	0.0263	-0.0080	3.91
<b>3·FIB</b>	I…Pd	0.0188	0.0416	-0.0088	4.30
<b>4·FIB</b>	I…Pt	0.0188	0.0416	-0.0111	5.42



## Electron localization function projections for (1–4)·2FIB



**Figure S4.** Electron localization function (ELF) projections with contour lines (0.1 step) along the S···S···I plane for the four model clusters. Bond (3, -1) critical points are blue, nuclear (3, -3) critical points are brown, ring (3, +1) critical points are orange, bond paths are white.

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