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Supplementary information

for

Pb…X (X = N, S, I) Tetrel Bonding Interactions in Pb(II) Complexes: Xray characterization, Hirshfeld surfaces and DFT calculations

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Branched Tube



Scheme S1. Representation of the branched tube used for the crystallization of compounds 1-4

Supramolecular structures (1-4).

The solid-state structure of **1** includes a combination of intermolecular weak C–H···O hydrogen bonds, π – π stacking and C–H··· π interactions (Tables S1 and S2). In the first substructure, the carbon atom C(7) acts as donor to the acetate oxygen atoms O(1A)ⁱ (symmetry code: i: 1-x, -y, -z); thus forming a centrosymmetric R₂²(10) dimer (M) centred at ½,0,0 position. In the opposite side of this dimer, the pyridine ring carbon atom C(3) acts as donor to the metal coordinating oxygen atom O(1)ⁱ (symmetry code: i: -x, -y, 1-z). Thus forming another centrosymmetric R₂²(10) dimeric ring (N) centred at 0,0,½ position. These two types of dimeric units lead the molecules to propagate along [100] direction (Fig. S1a). Finally, the pyridine ring carbon atom C(10) interconnect the dimeric layered motifs by connecting the O(1A)ⁱ (symmetry code: i: x, y, -1+z). The interconnection of the three weak C–H···O hydrogen bonds leads the molecules to generate a two-dimensional layered network in (101) plane (Fig. S1a). In another substructure, due the self-complementarity nature of the (N2/C2–C6) and (N4/C8–C12) rings, molecules are juxtaposed through face-to-face π -stacking interaction. These two rings from the parent and partner molecule forming a dimeric unit by π -stacking interaction, with an interplanar spacing of 3.309Å and a ring centroid separation of 3.5644 Å. This π -stacked dimer and the hydrogen bonded dimmers (M) and (N) leads the molecules to generate another layered assembly in (101) plane (Fig. S1b).



Fig. S1 (a) Formation of two-dimensional assembly in (101) plane generated through C–H···O hydrogen bonds; (b) Supramolecular network generated through hydrogen bonds and face-to-face π -stacking interactions.

The solid-state structure of **2** is stabilized through N–H···I, C–H···O, C–H···I bonds and π – π stacking interactions (Tables S1 and S2). Moreover, the structure exhibits Pb····I tetrel bonding interaction in the solid-state. In the first structure, the amide nitrogen atom N(9) acts as donor to the iodine atom I(1)ⁱ (symmetry code: i: x, -1+y, z); thus forming a centrosymmetric R₂²(20) dimeric ring (M) centred at 0,^{1/2},0 position. The dimeric M ring leads the molecules to propagate along [100] direction (Fig. S2a). In between two parallel chains, the pyridine ring carbon atom C(15) from the edge of the ligand acts as donor to the metal coordinated iodine atom I(2); thus again forming a centrosymmetric R₂²(12) dimeric ring (N) centred at 0,1,^{1/2} position. Due to the self-complementary nature, the dimeric ring (M) and (N) interconnect the molecules to generate a network in the (101) plane (Fig. S2a). In another substructure, the pyridine rings are juxtaposed through multi π -stacking with another (N17/C12–C16) ring of partner molecule with the ring centroid separations of 3.555(14)Å and 4.181(14)Å respectively. These multi π -stacking interactions lead the molecules to generate a layered assembly in (101) plane (Fig. S2b). Again, the

interconnection between two (N1/C2–C6) pyridine rings and (N17/C12–C16) rings leads the molecules to generate another supramolecular layered assembly in (011) plane (Fig. S2c).



Fig. S2 (a) Network structure generated by N–H···I and C–H···I bonding interactions; (b) Formation of layer network through π -stacking interactions; (c) Formation of another layer structure through Multi π -stacking interactions in (2).

Complex **3** crystallizes in triclinic space group $P\bar{i}$ and features a centrosymmetric acetate bridged tetranuclear Pb moiety. The Schiff base ligand coordinates two Pb ions (Pb1 and Pb2) and the acetate oxygen atom O2 and O3 are in inversion centre (symmetry code: -x, -y, -z+1) which generates the tetranuclear molecular moiety. The solid-state structure of (**3**) exhibits C–H···S, C–H···O bonds, π – π stacking and tetrel bonding interactions. The pyridine ring carbon atoms C(2) and C(9) acts as donor to the thiocyanate S(2) and acetate O(2) atoms in the molecules respectively. Moreover, the thiocyanate S(2) acts as double acceptor to the carbon atom C(7). Thus, forming an infinite one-dimensional chain along [010] direction (Fig. S3a). In another substructure, the pyridine ring (N1/C1–C5) is in contact with the ring centroid of another pyridine ring (N4/C8–C12), thus forming a dimeric fragment which leads the molecules to propagate along

[010] direction. Finally, the interconnection of the dimeric units through π - π stacking interaction (Table S2) between two (N4/C8–C12) rings of the parent and partner molecules defining well connected columns which forms a supramolecular stacked ribbon in **3**. The pyridine rings are strictly parallel, with ring centroid separation of 3.655(3)Å and interplanar spacing of 3.326(2)Å. The interconnection between two types of π -stacking interactions leads the molecules to generate a two-dimensional supramolecular network in (011) plane (Fig. S3b).



Fig. S3 (a) Formation of one-dimensional chain via hydrogen bonds; (b) Supramolecular layered network generated through multi π -stacking interactions in (3).

In the solid-state, the crystal structure of **4** is stabilized through N–H···N, O–H···S, N– H···O hydrogen bonds, π – π stacking and Pb···N, Pb···S tetrel bonding interactions. The N(2)–H group establishes an H-bonding interaction with the thiocyanate N(10) atom and the ethanol acts as both donor and acceptor *via* the O(3)–H connecting the thiocyanate S(2) atom and nitrogen atom N(7) of the ligand, thus forming an infinite chain along [100] direction (Fig. S4a). In addition, the pyridine rings (N1/C2–C6) and (N4/C8–C12) form face-to-face π -stacking interactions. The pyridine ring (N1/C2–C6) is juxtaposed to the centroid of the (N4/C8–C12) ring with an interplanar spacing of 3.318(2)Å and inter-centroid distance of 3.642(2)Å. The (N4/C8– C12) ring is again juxtaposed to the centroid of the (N1/C2–C6) ring with an inter-centroid separation distance 3.753(2)Å. These multi π – π stacking interactions generate a supramolecularlayered network in (**4**) (Fig. S4b).



Fig. S4 (a) 1D chain propagating along [100] direction through hydrogen bonds; (b) Layered assembly generated through π - π stacking interactions in (4).



Fig. S5 Hirshfeld surface mapped with d_{norm} for complexes (1–4) and are depicted in (*a*–*d*) respectively.



Fig. S6 Perspective view of the resolved d_{norm} surfaces corresponding to σ -hole contacts in (1–4).

D–H···A	D–H	H···A	D····A	D–H···A	Symm
Complex (1)					
С3-Н3…О1	0.95	2.31	3.036(3)	133	-x,-y,1-z
C7–H7…O1A	0.97(3)	2.50(3)	3.310(3)	142(2)	1-x,-y,-z
O10−H10···O1A	0.95	2.47	3.331(3)	150	x,y,-1+z
$C(2A)-H(2B)\cdots Cg(1)$		2.89	3.583(3)	128	1-x,-y,1-z
Complex-(2)					
N9–H9…I1	0.86	3.05	3.88(2)	164	x,-1+y,z
С6–Н6…О8	0.93	2.32	3.15(3)	149	-x,1-y,2-z
C16–H16…I2	0.93	3.05	3.76(2)	134	
Complex (3)					
C2-H2····S2	0.93	2.84	3.752(5)	166	-x,1-y,1-z
C7–H7…S2	0.93	2.83	3.654(6)	149	-x,1-y,1-z
С9–Н9…О2	0.93	2.48	3.357(7)	157	x,1+y,z
Complex (4)					
$N2-H2N\cdots N1$	0.86	2.30	2.653(4)	105	
N2−H2N···N10	0.86	2.32	3.108(5)	153	1-x,1-y,2-z
O3–H3O…S2	0.82	2.52	3.240(5)	147	-x,1-y,2-z
N7–H7N…O3	0.86	2.06	2.870(6)	156	
N7–H7N…N8	0.86	2.29	2.635(5)	104	
C12–H12····O2	0.93	2.42	3.063(5)	127	
C19–H19····O3	0.93	2.53	3.286(6)	139	
C24–H24…O1	0.93	2.40	3.075(6)	129	
1) is the centroid of the rings gene	s the centroid of the rings generated through the atoms (N2/C2–C6).				

 Table S1: Relevant Hydrogen Bonding Parameters in (1–4).

	asie szt Geometrical parameters (1,) for the to staching interactions.							
	rings <i>i-j</i>	$Rc^{[a]}$	$R1v^{[b]}$	$R2v^{[c]}$	$\alpha^{[d]}$	$\beta^{[e]}$	$\gamma^{[f]}$	Symmetry
			0	Complex (1)				
	Cg(1)···Cg(2)	3.5644 (13)	3.3092 (9)	3.4290(9)	6.02	15.85	21.81	-x, -y, -z
			0	Complex (2)				
	Cg(1)···Cg(1)	3.679 (15)	3.382(11)	3.382(11)	0.00	23.20	23.20	-x, -y, 2-z
	Cg(1)···· $Cg(1)$	3.687(15)	3.282(11)	3.282(11)	0.00	27.09	27.09	1-x, -y, 2-z
	Cg(2)···Cg(2)	3.555(14)	3.239(10)	3.239(10)	0.00	24.36	24.36	-x, 1-y, 1-z
	Cg(2)···Cg(2)	4.181(14)	3.292(10)	3.292(10)	0.00	38.08	38.08	1-x, 1-y, 1-z
			0	Complex (3)				
	Cg(1)···Cg(2)	3.643(3)	3.278(2)	3.330(2)	2.0	23.89	25.87	-x, 1-y, 1-z
	Cg(2)···Cg(2)	3.655(3)	3.326(2)	3.326(2)	0.0	24.48	24.48	-x, 1-y, -z
Complex (4)								
	Cg(1)···Cg(2)	3.642(2)	3.318(2)	3.487(2)	7.8	16.77	24.34	1-x, 1-y, 2-z
	$Cg(1)\cdots Cg(2)$	3.753(2)	3.326(2)	3.602(2)	12.0	16.32	27.61	x, 3/2-y, -1/2+z

Table S2. Geometrical parameters (Å, °) for the π -stacking interactions.

Cg(1) and Cg(2) are the centroids of the (N2/C2–C6) and (N4/C8–C12) rings respectively in complex (1); Cg(1) and Cg(2) are the centroids of the (N1/C2–C6) and (N17/C12–C16) rings respectively in complex (2); Cg(1) and Cg(2) are the centroids of the (N1/C1–C5) and (N4/C8–C12) rings respectively in complex (3); Cg(1) and Cg(2) are the centroids of the (N1/C2–C6) and (N4/C8–C12) rings respectively in complex (4). ^[a]Centroid distance between ring i and ring j. ^[b]Vertical distance from ring centroid i to ring j. ^[c]Vertical distance from ring centroid j to ring i. ^[d] Dihedral angle between the first ring mean plane and the second ring mean plane of the partner molecule. ^[e]Angle between the second ring mean plane of the partner molecule.

Contact	% of contribution	Contact	% of contribution	
Complex (1)		Complex (2)		
PB…N/N…PB	4.7	PB…N/N…PB	3.6/3.7	
PB···C/C···PB	0.4	PB…I/I…PB	3.2	
PB···H/H···PB	4.0	PB···H/H···PB	0.8	
O…H/H…O	19.3	O…H/H…O	7.5/7.4	
N…H/H…N	4.8	N…H/H…N	10.3/10.4	
С…Н/Н…С	10.4	I…H/H…I	33.5	
C···O/O···C	1.3	С…Н/Н…С	9.6/9.7	
C…N/N…C	5.4	I…N/N…I	0.8	
N····O/O····N	1.2	I…O/O…I	0.6/0.7	
NN	1.5	I…C/C…I	3.0	
С…С	6.8	C···N/ N···C	0.8	
Н…Н	40.0	С…С	8.2/8.1	
Others	0.2	Н…Н	18.1/17.8	
		Others	0.0	
			·	
Complex (3)		Complex (4)		
PB…N/N…PB	4.7	PB…N/N…PB	0.9	
PB…S/S…PB	2.1	PB···S/S···PB	0.7	
PB····O/O···PB	0.2	PB····C/C···PB	0.2	
PB····C/C···PB	1.7	PB···H/H···PB	0.3	
PB···H/H···PB	0.0	O…H/H…O	6.1	
O…H/H…O	5.5	N…H/H…N	14.0	
N…H/H…N	11.1	S…H/H…S	12.5	
S…H/H…S	13.4	С…Н/Н…С	20.7	
С…Н/Н…С	17.9	S…N/N…S	0.6	
S…N/N…S	1.4	S…O/O…S	0.2	
S····O/O····S	1.2	S…C/C…S	1.1	
S…C/C…S	1.3	CO/ OC	0.2	
С…О/ О…С	0.9	C···N/ N···C	3.8	
C…N/ N…C	3.6	N…O/ O…N	0.0	
N…O/ O…N	1.2	N…N	1.1	
N…N	1.4	С…С	6.9	
С…С	5.8	Н…Н	30.7	
Н…Н	26.3	Others	0.0	
Others	0.3			

Table S3. Percentage contributions of inter-atomic contacts to the Hirshfeld surface.