Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Extended lead(II) architectures engineered via tetrel bonding interactions

Ghodrat Mahmoudi,*[a] Ennio Zangrando,[b] Mariusz P. Mitoraj,*[c] Atash V. Gurbanov,[d] Fedor I. Zubkov,[e] Maryam Moosavifar,[a] Irina A. Konyaeva,[f,g] Alexander M. Kirillov*[h] and Damir A. Safin*[i]

[a]*Department of Chemistry, Faculty of Science, University of Maragheh, P.O. Box 55181-83111, Maragheh, Iran. E-mail: mahmoudi_ghodrat@yahoo.co.uk*

[b]*Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy*

[c]*Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R.Ingardena 3, 30-060 Cracow, Poland. E-mail: mitoraj@chemia.uj.edu.pl*

[d]*Department of Chemistry, Baku State University, Z. Khalilov Str. 23, AZ1148, Baku, Azerbaijan*

[e] *Organic Chemistry Department, Faculty of Science, Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., Moscow, 117198, Russian Federa*

[f]*Limited Liability Company «NIOST», Kuzovlevski trakt 2, 634067, Tomsk, Russian Federation*

[g]*Department of Technology of Organic Substances and Polymer Materials, National Research Tomsk Polytechnic University, Lenin ave. 43, 634050 Tomsk, Russian Federation*

[h]*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal. E-mail: kirillov@ist.utl.pt*

[i]*Institute of Chemistry, University of Tyumen, Perekopskaya Str. 15a, 625003 Tyumen, Russian Federation. E-mail: damir.a.safin@gmail.com, d.a.safin@utmn.ru*

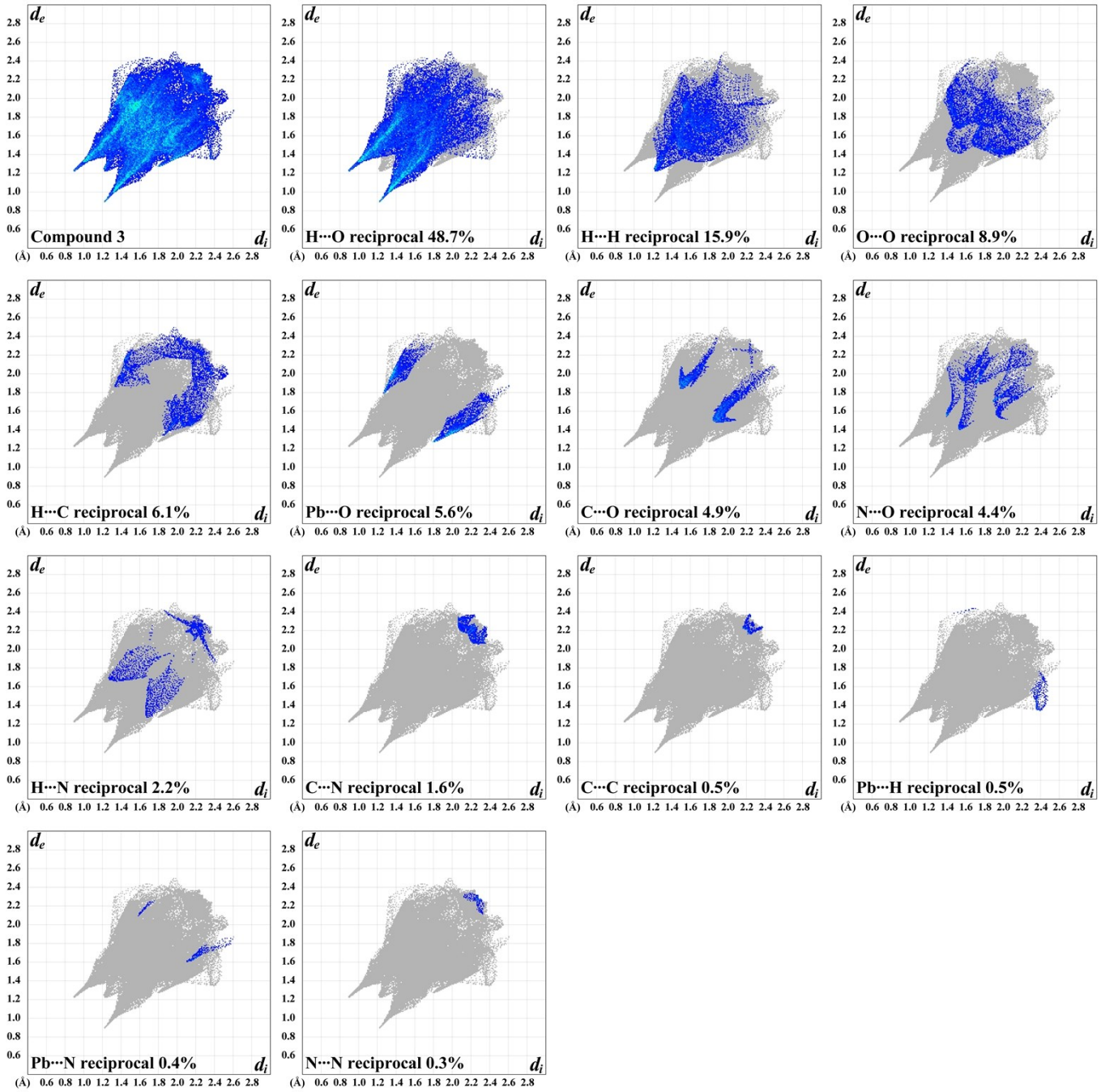
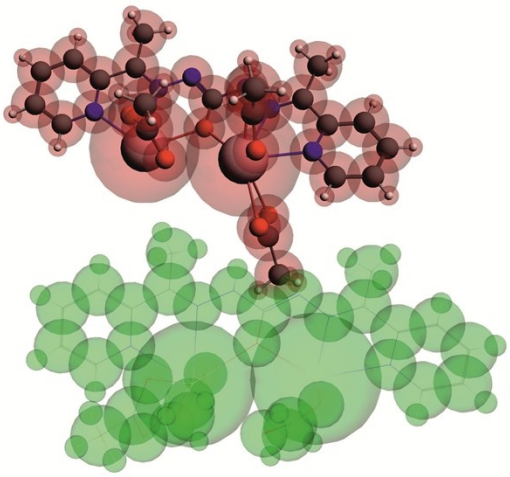
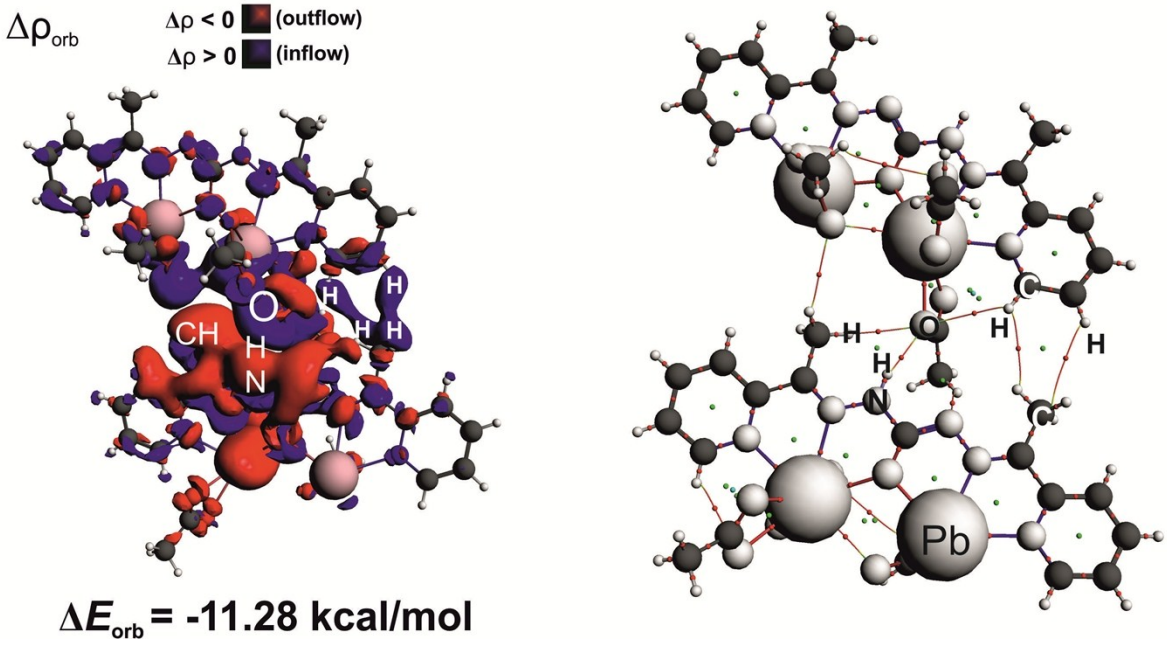


Fig. S1. 2D and decomposed 2D fingerprint plots of observed contacts for **3**.



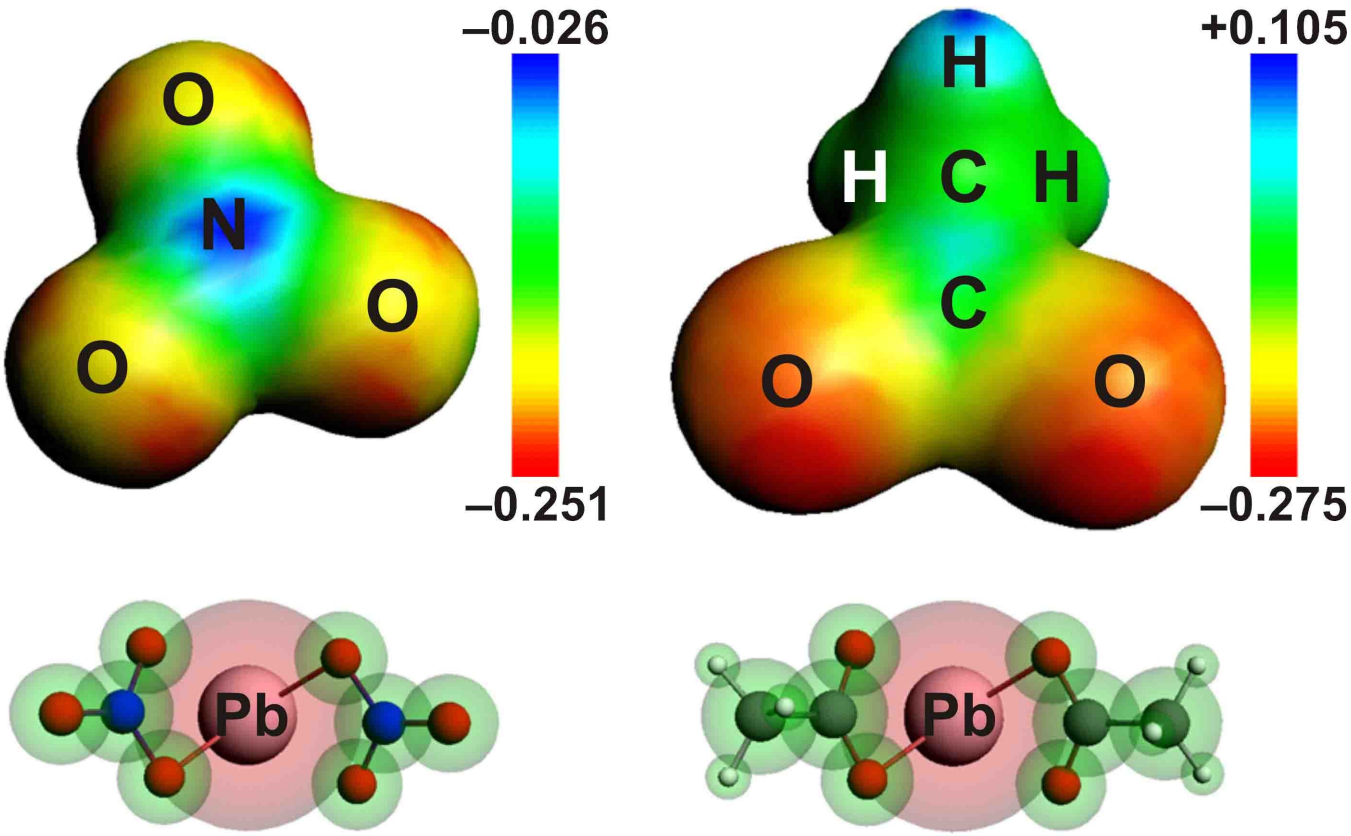
	NH-O/CH-O/CH-HC
ΔE_{int}	-20.26
ΔE_{elstat}	-15.45
ΔE_{orb}	-11.28
$\Delta E_{dispersion}$	-14.50
ΔE_{Pauli}	20.97

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{orb} + \Delta E_{dispersion} + \Delta E_{Pauli}$$



ΔE_{orb} = -11.28 kcal/mol

Fig. S2. (Top) Cluster model of **3** together with the fragmentation pattern applied in the ETS-NOCV analysis. (Bottom) The overall deformation density $\Delta\rho_{orb}$ with the corresponding orbital interaction energies ΔE_{orb} as well as the QTAIM molecular graph demonstrating formation of NH-O, CH-O and CH-HC charge delocalizations.



	$Pb–ONO_2$	$Pb–OC(O)CH_3$
ΔE_{int}	–540.49	–588.06
ΔE_{elstat}	–519.27	–549.00
ΔE_{orb}	–147.31	–168.54
$\Delta E_{dispersion}$	–1.46	–1.20
ΔE_{Pauli}	127.56	130.68

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{orb} + \Delta E_{dispersion} + \Delta E_{Pauli}$$

Fig. S3. (Top) Molecular electrostatic potentials for NO_3^- and CH_3COO^- (DFT/ADF/BLYP-D3/TZP). (Bottom) The ETS-NOCV results describing bonding between Pb^{II} and the corresponding anion.

Table S1. Selected bond lengths (Å) and angles (°) for **1** and **2**

	1	**2**
$Pb–N_{2\text{-}Py}$	2.679(2)	2.732(6)
$Pb–N_{3\text{-}Py}$	2.695(2)	2.894(7)
$Pb–N_{imine}$	2.602(2)	2.659(6)
$Pb–O_{C=O}$	2.679(2)	2.499(5)
$Pb–O_{nitrate/methoxide}$	2.504(2), 2.640(2), 2.778(2), 2.826(2)	2.187(5)
$Pb\cdots O_{tetrel}$	3.117(2)	—

Table S2. Selected bond lengths (Å) and angles (°) for **3** and **4**

	3	**4**	
		Pb(1)	Pb(2)
$Pb–N_{2\text{-}Py}$	2.492(10)	2.535(3)	2.563(4)
$Pb–N_{imine}$	2.563(11)	2.480(3)	2.700(4)
$Pb–O_{C=O}$	2.619(7)	2.445(3)	2.599(3)
$Pb–O_{nitrate/acetate}$	2.430(13), 2.655(11), 2.755(10)	2.338(3), 2.787(3)	2.552(3), 2.613(3), 2.626(3), 2.729(4), 2.916(3)
$Pb\cdots O_{tetrel}$	3.061(11), 3.091(13), 3.275(13), 3.353(13)	2.995(3), 3.518(3)	—
$Pb\cdots N_{tetrel}$	—	3.143(4)	—

Table S3. Classic hydrogen bond lengths (Å) and angles (°) for **1**, **3** and **4**

	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
1[a]	N(3)–H(3N)···O(5)	0.82(3)	2.00(3)	2.787(3)	160(3)
3[b]	N(3)–H(3N)···O(5)[#1]	0.86	2.45	3.025(16)	124
	N(3)–H(3N)···O(6)[#2]	0.86	2.24	3.044(16)	155
4[c]	N(4)–H(4N)···O(7)	0.88	1.98	2.837(5)	165

[a]Symmetry transformations used to generate equivalent atoms: *x*, –1/2 – *y*, 1/2 + *z*.

[b]Symmetry transformations used to generate equivalent atoms: #1: 1 – *x*, 1 – *y*, 1 – *z*; #2: –*x*, 1 – *y*, 1/2 + *z*.

[c]Symmetry transformations used to generate equivalent atoms: 1 – *x*, 1/2 + *y*, 3/2 – *z*.

Table S4. π···π interaction distances (Å) and angles (°) for **1** and **2**[a]

Complex	Cg(*I*)	Cg(*J*)	*d*[Cg(*I*)–Cg(*J*)]	α	β	γ	slippage
1[b]	Cg(1)	Cg(1)[#1]	3.5258(15)	0.00(13)	13.9	13.9	0.846
	Cg(2)	Cg(2)[#2]	3.7395(15)	0.02(12)	28.0	28.0	1.757
	Cg(2)	Cg(2)[#3]	3.6520(15)	0.02(12)	25.0	25.0	1.544
2[c]	Cg(4)	Cg(5)[#1]	3.707(5)	10.5(4)	19.8	26.3	1.256
	Cg(4)	Cg(5)[#2]	3.898(5)	10.5(4)	33.7	26.7	2.164
	Cg(5)	Cg(4)[#3]	3.898(5)	10.5(4)	26.7	33.7	1.754
	Cg(5)	Cg(4)[#4]	3.707(5)	10.5(4)	26.3	19.8	1.642

[a]Cg(*I*)–Cg(*J*): distance between ring centroids; α: dihedral angle between planes Cg(*I*) and Cg(*J*); β: angle Cg(*I*) → Cg(*J*) vector and normal to plane *I*; γ: angle Cg(*I*) → Cg(*J*) vector and normal to plane *J*; slippage: distance between Cg(*I*) and perpendicular projection of Cg(*J*) on ring *I*.

[b]Symmetry transformations used to generate equivalent atoms: #1 –*x*, –*y*, –*z*; #2 1 – *x*, –1 – *y*, 1 – *z*; #3 1 – *x*, –*y*, 1 – *z*. Cg(1): N(1)–C(8)–C(9)–C(10)–C(11)–C(12), Cg(2): N(4)–C(3)–C(2)–C(6)–C(5)–C(4).

[c]Symmetry transformations used to generate equivalent atoms: #1 –1 + *x*, –1 + *y*, *z*; #2 *x*, –1 + *y*, *z*; #3 *x*, 1 + *y*, *z*; #4 1 + *x*, 1 + *y*, *z*. Cg(4): N(1)–C(8)–C(12)–C(11)–C(10)–C(9), Cg(5): N(4)–C(5)–C(6)–C(7)–C(8)–C(9).