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Supplementary Information for manuscript:

Concurrent Agostic and Tetrel bonding interactions in Lead(II) complexes with a isonicotinohydrazide based ligand and several anions

Ghodrat Mahmoudi,[a]* Antonio Bauzá,[b] and Antonio Frontera[b,]*

[a]*Department of Chemistry, Faculty of Science, University of Maragheh, P.O. Box 55181-83111, Maragheh, Iran*
[b]*Departament de Química, Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), SPAIN*

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1. Experimental

1.1. Materials

High purity N'-(phenyl(pyridin-2-yl)methylene)isonicotinohydrazide were prepared using the synthetic method available in the literature.[1] Lead(II) chloride, lead(II) iodide, lead(II) nitrite, ammonium thiocyanate were purchased from commercial sources and were used as received. All other chemicals and solvents used were AR grade.

1.2. Physical measurements

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer. Microanalyses were performed using a Heraeus CHN-O-Rapid analyzer.

1.3. Preparation of the complexes

Compounds **1-4** were obtained from methanolic solutions using a pre-assigned molar ratios of appropriate lead(II) salt, a Schiff base, N'-(phenyl(pyridin-2-yl)methylene)isonicotinohydrazide (**L**) and different anions (halides/pseudohalides/nitrite) at room temperature The typical syntheses of **1-4** are described below.

*1.3.1. [Pb(L)(Cl)]CH_3OH (**1**), [Pb(L)(I)] (**2**) and [Pb(L)(μ-NO_2)]CH_3OH (**4**)*

To a methanolic solution (10 ml) of $PbCl_2$ (0.0278 g, 0.1 mmol), **L** (0.0302 g, 0.1 mmol) in MeOH in the same solvent (5 ml) was slowly added in succession at room temperature and the resulting reaction mixture was left undisturbed in open air for slow evaporation. After a few days light yellow microcrystals of **1** were collected and dried *in vacuo* over silica gel indicator. Compounds **2** and **4** were prepared similarly using the same stoichiometry and reaction condition except that PbI_2 (0.0461 g, 0.1 mmol) or $Pb(NO_2)_2$ (0.0299 g, 0.1 mmol) instead of $PbCl_2$ was used, respectively.
Anal. Calc. for $C_{38}H_{34}N_8O_4Cl_2Pb_2$ (**1**): C, 39.5; H, 3.1; N, 9.7. Found: C, 39.6; H, 2.9; N, 9.8%. Yield: 0.089 g (78%). IR (KBr, cm^{-1}): ν(CO) 1619; ν(C=N) 1509; ν(C=N) + ν(C=C) 1547,
Anal. Calc. for $C_{38}H_{30}N_8O_4I_2Pb_2$ (**2**): C, 34.3; H, 2.3; N, 8.4. Found: C, 34.2; H, 2.4; N, 8.8%. Yield: 0.073 g (55%). IR (KBr, cm^{-1}): ν(CO) 1617; ν(C=N) 1503; ν(C=N) + ν(C=C) 1564.
Anal. Calc. for $C_{19}H_{17}N_5O_4Pb$ (**4**): C, 38.9; H, 2.9; N, 11.9. Found: C, 38.1; H, 2.2; N, 12.3%. Yield: 0.039 g (67%). IR (KBr, cm^{-1}): ν(C=N) 1499; ν(C=N) + ν(C=C) 1572.

*1.3.2. [Pb(L)(NCS)]$_2$ (**3**)*

L (0.0302 g, 0.1 mmol) in methanol (10 ml) was added dropwise to a solution of $PbCl_2$ (0.0278 g, 0.1 mmol) dissolved in the same solvent (10 ml). To this resulting yellow solution, a methanolic solution of NH_4SCN (0.0076 g, 0.1 mmol) (5 ml) was added slowly stirring for 45 min at room temperature. The final light yellow solution was processed as in **1** to get light yellow rectangular single crystals of **3**.
Anal. Calc. for $C_{38}H_{26}N_{10}O_2S_2Pb_2$ (**3**): C, 40.3; H, 2.3; N, 12.4. Found: C, 41.1; H, 2.1; N, 11.8%. IR (KBr, cm^{-1}): ν = CH b (oop): 697 (m) and 789 (m); CH b: 1305(m); CCst: 1450 (m); C=N st: 1506 and 1561 (m); C=O st (Ligand) 1640; S-CN st: 2066 (s); CH st: 3057 (w), and OH st: 3444 (w) cm^{-1} .

1.4. X-ray crystallographic analyses

Diffraction data of the single crystals of **1-4** were collected at 100–173 K on a (Nonius Kappa CCD FR590 single crystal diffractometer using graphite monochromated Mo-Kα radiation. The unit cell parameters were obtained from SAINT[2] and absorption corrections were performed with SADABS.[3] The structures were solved by direct methods and refined by full-matrix least-squares method based on F^2 using SHELXTL.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were fixed geometrically and refined using a riding model. A small portion of the collected reflections was therefore rejected assuming to be incorrectly measured. Despite this, the structures were refined using 95% of the possible data, which were adequate to give a precise structure. All calculations were carried out using SHELXTL, PLATON[5] and Mercury 2.3[6] programs. A summary of the crystallographic data and structure determination parameters is given in Table S1.

Table S1. Crystallographic data and structure refinement parameters for **1-4**

Crystal parameters	**1**	**2**	**3**	**4**
Chemical formula	$C_{38}H_{34}N_8O_4Cl_2Pb_2$	$C_{38}H_{30}N_8O_4I_2Pb_2$	$C_{38}H_{26}N_{10}O_2S_2Pb_2$	$C_{19}H_{17}N_5O_4Pb$
Formula mass	1152.03	1330.88	1133.23	586.57
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P21/c (No. 14)	P21/c (No. 14)	P212121 (No. 19)	P21/c (No. 14)
a/Å	10.6380(11)	10.9595(9)	8.8580(2)	10.7519(11)
b/Å	19.076(2)	19.2524(11)	19.6630(5)	19.718(2)
c/Å	9.2825(10)	9.5858(8)	21.1860(7)	9.2550(9)
α^0	90	90	90	90
β°	103.396(2)	105.181(9)	90	105.250(4)
γ^0	90	90	90	90
V/Å^3	1832.5(3)	1952.0(3)	3690.07(17)	1893.0(3)
λ/Å	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}/g cm^{-3}	2.088	2.264	2.040	2.058
Z	2	2	4	4
T/K	100(2)	173 (2)	110(2)	100(2)
μ (mm^{-1})	9.376	10.246	9.277	8.950
F(000)	1096	1232	2144	1120
Crystal size (mm^3)	0.32 ×0.38×0.51	0.10 ×0.15×0.20	0.20 ×0.30×0.50	0.10 ×0.11×0.12
θ ranges (°)	2.0 to 31.0	4.4 to 27.5	2.1 to 27.5	2.5 to 27.5
h/k/l	-15/14, -27/27, -12/13	-14/14, -25/25, -12/13	-9/11, -24/25, -22/27	-13/13, -25/25, -11/12
Reflections collected	13654	12547	8371	4332
Independent reflections	5424	4299	6052	4141
Data/restraints/parameters	5424/8/261	4299/7/246	6052/0/488	4141/0/264
R_{int}	0.026	0.059	0.083	0.031
Final R1 values [$I>2\sigma(I)$]	0.0227	0.0588	0.0450	0.0146
Final wR(F^2) values [$I>2\sigma(I)$]	0.0497	0.1666	0.0923	0.0135
Final R1 values (all data)	0.0281	0.0809	0.0737	0.0345
Final wR(F^2) values (all data)	0.0514	0.1758	0.1012	0.0340
Goodness of fit on F^2	1.039	1.036	0.958	0.973
Largest peak and hole (eÅ^{-3})	1.44 and -0.87	3.307 and -2.554	5.88 and -1.44	0.837 and -0.515

Weighting scheme: $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, calcd $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; x = 0.0218; y = 1.1812 (for **1**), x = 0.0984 (for **2**) and x = 0.01930; y = 2.3811 (for **3**); where $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Selected bond distances (Å), bond angles (°) and non-covalent forces for **1**-**3**.

Compound	Bond distances		Bond angles	
1	Pb1-Cl4	2.6463(8)	Cl4-Pb1-O1	88.26(5)
	Pb1-O1	2.4468(19)	Cl14-Pb1-N1	83.19(6)
	Pb1-N2	2.420(2)	Cl14-Pb1-N2	92.28(6)
	Pb1-N3_a	2.994(2)	Cl14-Pb1-N3_a	167.09(5)
	N2-N3	1.379(3)	O1-Pb1-N1	129.41(7)
			O1-Pb1-N2	65.42(8)
			O1-Pb1-N3_a	87.49(7)
			N1-Pb1-N2	65.24(8)
			N1-Pb1-N3_a	90.12(7)
			N2-Pb1-N3_a	74.87(7)
2	Pb1-I2	2.9809(10)	I2-Pb1-O1	88.5(2)
	Pb1-O1	2.461(8)	I2-Pb1-N1	90.3(2)
	Pb1-N2	2.416(9)	I2-Pb1-N3	83.5(2)
	Pb1-N1_a	2.966(10)	I2-Pb1-N1_a	166.41(18)
	N2-N3	1.386(13)	O1-Pb1-N2	65.7(3)
			O1-Pb1-N3	130.1(3)
			O1-Pb1-N1_a	87.9(3)
			N2-Pb1-N3	65.1(3)
			N1_a-Pb1-N2	76.3(3)
			N1_a-Pb1-N3	88.9(3)
3	Pb1-O1	2.431(6)	O1-Pb1-N1	129.0(2)
	Pb1-N1	2.551(9)	O1-Pb1-N2	66.0(2)
	Pb1-N2	2.411(8)	O1-Pb1-N5	83.4(3)
	Pb1-N5	2.440(10)	O1-Pb1-N8	84.3(2)
	Pb1-N8	2.930(8)	N1-Pb1-N2	64.9(3)
	Pb2-O2	2.444(6)	N1-Pb1-N5	80.6(3)
	Pb2-N3	2.923(8)	N1-Pb1-N8	93.9(2)
	Pb2-N6	2.523(8)	O2-Pb2-N3	84.7(2)
	Pb2-N7	2.421(7)	O2-Pb2-N6	128.4(2)
	Pb2-N10	2.404(10)	O2-Pb2-N7	65.7(2)
	S1-C19	1.616(14)	O2-Pb2-N10	83.3(3)
	S2-C38	1.585(13)	N3-Pb2-N6	93.9(2)
			N3-Pb2-N7	72.8(2)
			N3-Pb2-N10	159.2(3)
			N6-Pb2-N7	64.7(2)
			N6-Pb2-N10	80.4(3)
			N7-Pb2-N10	86.8(3)
	Pb1-O1	2.4681(14)	O1-Pb1-O2	74.80(5)
	Pb1-O2	2.4226(17)	O1-Pb1-O3	116.31(5)
	Pb1-O3	2.777(2)	O1-Pb1-N1	130.01(5)
	Pb1-N1	2.4821(18)	O1-Pb1-N2	65.19(5)
	Pb1-N2	2.4149(16)	O1-Pb1-N3_a	90.22(5)
	Pb1-N3_a	2.9438(17)	O2-Pb1-O3	46.89(5)

4	O2-N5	1.280(3)	O2-Pb1-N1	85.52(6)
	O3-N5	1.223(3)	O3-Pb1-N2	76.85(5)
			O2-Pb1-N3_a	151.78(5)
			O3-Pb1-N1	75.53(6)
			O3-Pb1-N2	113.12(6)
			O3-Pb1-N3_a	153.42(5)
			N1-Pb1-N2	65.75(5)
			N1-Pb1-N3_a	86.25(5)
			N2-Pb1-N3_a	75.15(5)
			O2-N5-O3	113.5(2)

Symmetry code: [a]1-x,1-y,1-z for **1**; [a]1-x,-y,1-z for **2**; [a]x,1/2-y for **3**

2. Theoretical methods:

The energies of all complexes included in this study were computed at the BP86-D3/def2TZVP level of theory. We have used the crystallographic coordinates for the theoretical analysis of the noncovalent interactions present in the solid state. The calculations have been performed by using the program TURBOMOLE version 7.0.[7] The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique.[8] For the calculations we have used the DFT-D functional with the latest available correction for dispersion (D3).[9] The molecular electrostatic potential (MEP) surfaces and NBO analyses have been performed at the BP86/def2TZVP level of theoryby means of the Gaussian09 package.[10] The Bader's "Atoms in molecules" theory has been used to study the interactions discussed herein by means of the AIMall calculation package.[11]

3. Figures S1 and S2:

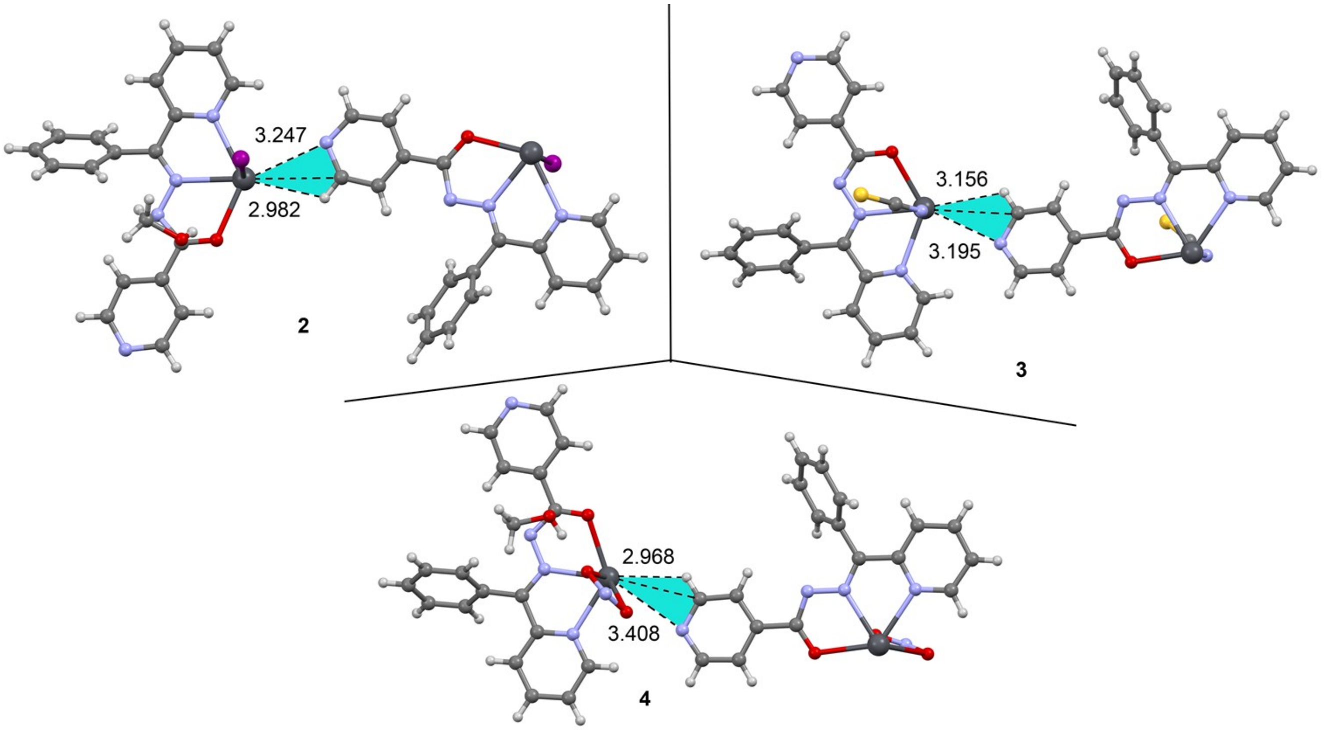

Fig. S1 Partial view of the X-ray solid state structures of compounds **2**-**4** with indication of the concurrent tetrel bonding and agostic interactions. Distances in Å

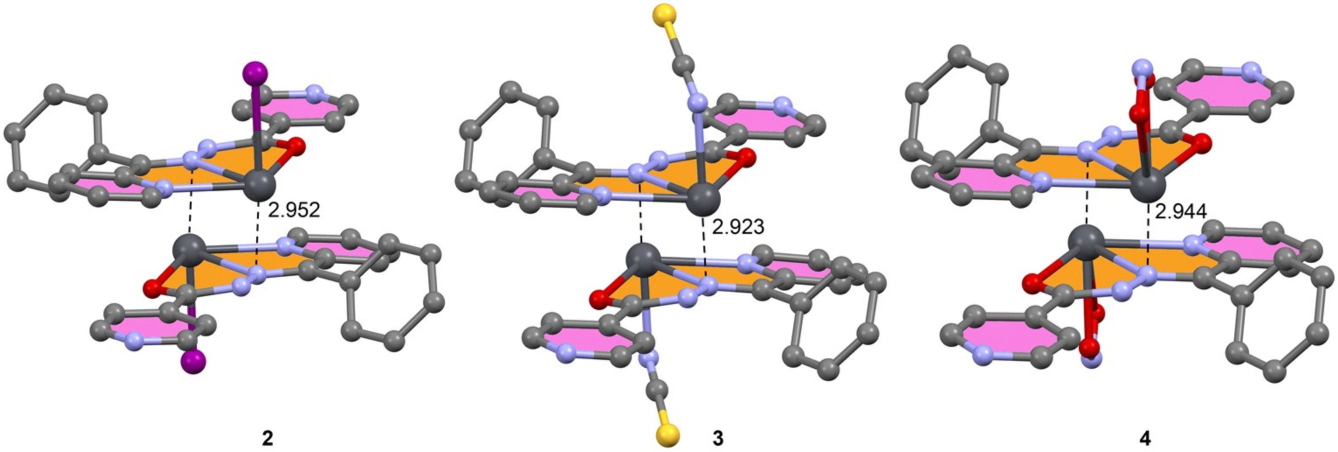

Fig. S2 Partial view of the X-ray solid state structures of compounds **2**-**4** with indication of the chelate ring–chelate ring interactions Distances in Å

4. References

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