"Supporting Information"

Novel mixed anion [*trans*-Pt(C≡CTol)₂(CN)₂] as building block of new luminescent Pt^{II}-Tl^I and Pt^{II}-Pb^{II} coordination polymers.

Jesús R. Berenguer, Julio Fernández, Elena Lalinde* and Sergio Sánchez.

Departamento de Química - Grupo de Síntesis Química de La Rioja, UA - C.S.I.C.

Universidad de La Rioja, 26006, Logroño, Spain

* Corresponding author. E-mail: elena.lalinde@unirioja.es.

Experimental Section

Materials and methods.

Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer. IR spectra were recorded on a Nicolet Nexus FT-IR Spectrometer from Nujol mulls between polyethylene sheets. Complex **1** is the only soluble enough to register its ¹H and ¹³C NMR spectra, being recorded on a Bruker ARX 300 spectrometer; chemical shifts are reported in ppm relative to external standars (TMS and CFCl₃ respectively) and coupling constants in Hz. MALDI-TOF spectra was recorded on a Microflex MALDI-TOF Bruker spectrometer operating in the linear and reflector modes using dithranol (DIT) as matrix. The Molar Conductivity of complex **1** was measured in acetone solution (5×10^{-4} M) using a Crison GLP31 conductimeter. UV-Vis spectrum of complex **1** was recorded on a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter. The lifetime measurements were performed operating in the phosphorimeter mode (with a F1-1029 lifetime emission PMT assembly, using a 450 W Xe lamp). [*trans*-Pt(C=CTol)₂(PPh₃)₂]¹ and K(HBpz₃)² were prepared as reported and other reagents were obtained from commercial sources.

Computational details for DFT calculations. All DFT calculations were carried out using the Gaussian 03^3 package applying the Becke's 3-parameter hybrid function combined with the Lee-Yang-Parr correlation function (B3LYP).⁴ The basis set used was the LanL2DZ effective core potential⁵ for the metal centers (Pt, Tl and Pb) and 6-31G(d,p) for the ligand atoms. The anion [*trans*-Pt(C=CTol)₂(CN)₂]²⁻ of complex **1** was optimized under vacuum by isolating it from the X-ray structure of **2**. No negative values were found in the results of the vibrational frequency analysis. Single point

calculations were performed on $\{trans-PtTl_2(C=CTol)_2(CN)_2\}$ and $\{[trans-Pt(C=CTol)_2(CN)_2][(PbTp)(acetone)_2]\}$ using the geometries obtained from the X-ray structures of complexes 2 and 3, respectively, keeping all distances, angles and dihedral angles frozen.

Preparation of (NBu₄)₂[trans-Pt(C=CTol)₂(CN)₂] (1). (NBu₄)CN (0.268 g, 1 mmol) was added to a suspension of *trans*-Pt(C=CTol)₂(PPh₃)₂ (0.475 g, 0.5 mmol) in acetone. After one hour stirring at room temperature a yellow solution is obtained. The solvent was removed in vacuum and the yellow oily residue treated with ~ 30 ml of Et₂O. The mixture was stirred for 1 h, dissolving the free PPh₃ and yielding the precipitation of 34 as a pale-yellow solid. The solid was filtered off and repeatedly washed with Et₂O (0.414 g, 86%). Anal. Calcd for C₅₂H₈₆N₄Pt (962.36): C, 64.90; H, 9.01; N, 5.82. Found: C, 64.85 H, 8.74 N, 6.02. MS MALDI(-): m/z 719.3 ([M-NBu₄], 49%), 477.0 $([M-2NBu_4]^{-}, 100\%)$. IR (cm⁻¹): v(C=N) 2114 (vs), v(C=C) 2093 (vs). ¹H NMR (δ , 300.13 MHz, CDCl₃, 293 K): 7.15 (d, J = 7.8 Hz, 4H, C₆H₄, Tol), 6.90 (d, J = 7.8 Hz. 4H, C₆H₄, Tol), 3.43 (m, 16H, NCH₂, NBu₄), 2.23 (s 6H, CH₃, Tol), 1.66 (m, 16H, CH₂, NBu₄), 1.50 (m, 16H, CH₂, NBu₄), 0.94 (t, 24H, CH₃, NBu₄). ¹³C{¹H} NMR (δ, 100.14 MHz, CD₃COCD₃, 293 K): 133.0 (s, C⁴, Tol), 131.8 (s, CH, ${}^{4}J_{C-Pt} \approx 9$ Hz, Tol), 129.7 (s, C¹, ${}^{3}J_{C-Pt} \approx 24$ Hz, Tol), 129.7 (s, C-CN, ${}^{1}J_{C-Pt} = 1029$ Hz, CN), 129.1 (s, CH, Tol), 111.9 (s, ${}^{1}J_{C-Pt} = 934 \text{ Hz}, C_{\alpha}, C \equiv C$), 104.0 (s, ${}^{2}J_{C-Pt} = 255 \text{ Hz}, C_{\beta}, C \equiv C$), 59.6 (s, N-CH₂, NBu₄), 24.9 (s, -CH₂-, NBu₄), 21.3 (s, -CH₃, Tol), 20.5 (s, -CH₂-, NBu₄), 14.2 (s, -CH₃, NBu₄). $\Lambda_{M}((CH_{3})_{2}CO)$: 174.5 $\Omega^{-1} \cdot cm^{2} \cdot mol^{-1}$.

Preparation of {[*trans-,trans*-PtTl₂(C=CTol)₂(CN)₂]·2 MeOH} (2). (NBu₄)₂[*trans*-Pt(C=CTol)₂(CN)₂] 1 (0.050 g, 0.052 mmol) and TlPF₆ (0.036 g, 0.104 mmol) slowly diffuses in MeOH (~ 10 ml) at -30°C. After several days (up to 7), small yellow crystals

are obtained. Those crystals are filtered off, washed with MeOH, dried to air and labelled as **2** (0.020 g, 43%). Anal. Calcd for $C_{22}H_{22}N_2O_2PtTl_2$ (950.27): C, 27.81; H, 2.33; N, 2.95. Found: C, 28.00 H, 2.56 N, 3.05. MALDI(-): m/z 1567.6 ([Pt₂(C=CTol)₄(CN)₄Tl₃]⁻, 100%), 681.0 ([Pt(C=CTol)₂(CN)₂Tl]⁻, 35%). MALDI(+):

m/z 1090.9 ([Pt(C=CTol)₂(CN)₂Tl₂]⁺, 50%), 949.9 ([M]⁺, 10%). IR (cm⁻¹): ~ 2112 (s, overlap between v(C=N) and v(C=C)). The low solubility of this complex precludes its characterisation by NMR spectroscopy.

Preparation of {[*trans*-Pt(C=CTol)₂(CN)₂][(PbTp)(acetone)]₂} (3). KTp (0.066 g, 0.261 mmol) (Tp = trispyrazolylborate) is added to a solution of Pb(ClO₄)₂· 3H₂O (0.120 g, 0.261 mmol) in acetone (~ 10 ml) and the mixture stirred for ~ 15 min. at room temperature. After this time, (NBu₄)₂[*trans*-Pt(C=CTol)₂(CN)₂] **1** (0.125 g, 0.131 mmol) is added to the reaction pot, what causes the precipitation of **3** as a white solid which is filtered, washed with acetone and air dried (0.130 g, 66 %). Anal. Calcd for C₄₄H₄₆N₁₄B₂O₂Pb₂Pt (1434.04): C, 36.85; H, 3.23; N, 13.67. Found: C, 36.72 H, 3.45 N, 13.32. MALDI(-): *m/z* 1737.6 ([Pt₂(C=CTol)₄(CN)₄Pb₃Tp]⁻, 32%), 897.0 ([Pt(C=CTol)₂(CN)₂ PbTp]⁻, 100%). MALDI(+): *m/z* 1737.6 ([M – 2acetone + PbTp]⁺, 52%), 420.9 ([PbTp]⁺, 100%). IR (cm⁻¹): v(C=N) 2104 (s), v(C=C) 2097 (s). ¹H NMR (δ, 300.13 MHz, CD₂Cl₂, 293 K): 8.04 (s, 6H, pz, Tp), 7.90 (s, 6H, pz, Tp), 7.08 (s br, 4H, C₆H₄, Tol), 6.93 (d br, *J* ~ 6 Hz, 4H, C₆H₄, Tol), 2.30 (s, 6H, CH₃, Tol), 2.22 (s, 12H, CH₃, acetone).

X-ray Crystallography. Table S1 and S2 reports details of the structural analysis for complexes **2** and **3**, together with selected ORTEP views (ellipsoids are drawn at the 50% probability level). Yellow crystals of complex **2** were obtained by slow diffusion of a solution of TIPF₆ in MeOH at -30°C into a solution of $(NBu_4)_2[trans-$

Pt(C=CTol)₂(CN)₂] 1 in a mixture MeOH:CH₂Cl₂. Yellow crystals of complex 3 were obtained by slow diffusion of acetone in a saturated solution of the compound in CH₂Cl₂. X-ray intensity data has been collected with a NONIUS-KCCD area-detector diffractometer, using graphite-monochromated Mo K_{α} radiation (λ (MoK $_{\alpha}$) 0.71071 Å) and the images were processed using the DENZO and SCALEPACK suite of programs.⁶ The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-97.⁷ The absorption correction were performed using $XABS^{8}$ (2) or MULTI-SCAN⁹ (3). All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters of 1.2 times the U_{iso} value of their attached carbons for aromatic and methylene hydrogens and 1.5 times for the methyl groups. For complex 3, the hydrogen atom H1 directly bonded to B was assigned from the Fourier Map. For complex 3, one half molecule of H_2O was found in the asymmetric units. Also, three restrains have been used to model the acetone molecule in 3. The structures present some residual peaks greater than $1 e^{-A^{-3}}$ in the vicinity of the metal atoms or solvent molecules, but with no chemical meaning.

	2	$3 \cdot H_2O$
Empirical formula	$C_{22}H_{20}N_2O_2PtTl_2$	$C_{44}H_{48}B_2N_{14}O_3Pb_2Pt$
F_{w}	948.23	1452.05
T (K)	173(1)	173(1)
crystal system, space group	Triclinic, P-1	Triclinic, P-1
a(Å)	6.2450(3)	7.7464(6)
b(Å)	7.3320(3)	11.2992(7)
c(Å)	13.4130(6)	15.3002(12)
$\alpha(\text{deg})$	87.875(3)	71.013(4)
$\beta(deg)$	86.713(3)	89.708(3)
$\gamma(\text{deg})$	70.242(2)	79.895(4)
volume (A ³)	576.95(4)	1244.75(16)
Ζ	1	1
D_{calcd} (Mg/m ³)	2.729	1.934
absorption coefficient (mm ⁻¹)	19.996	9.602
F(000)	422	684
θ range for data collection (deg)	4.11 to 25.02	3.52 to 25.02
no of data // restraints // params	1999 // 0 // 135	4373 // 3 // 309
goodness-of-fit on $F^{2[a]}$	1.111	1.043
final R indexes $[I>2\sigma(I)]^{[a]}$	$R_1 = 0.0518, wR_2 = 0.1365$	$R_1 = 0.0392, wR_2 = 0.0881$
R indexes (all data) ^[a]	$R_1 = 0.0554, wR_2 = 0.1411$	$R_1 = 0.0575, wR_2 = 0.0959$
largest diff peak and hole (e.Å $^{-3}$)	4.156 and -4.078	2.184 and -1.682

 $\frac{1}{[a]} R1 = \sum (|F_o| - |F_c|) / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}; \text{ goodness of fit} = \{\sum [w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})\}^{1/2}; w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}; P = [\max(F_o^2; 0 + 2F_c^2] / 3.$

Table S2: Selected Bond Lengths [Å] and Angles [deg] for 2 and $3 \cdot H_2O$.						
			2			
Pt1-Tl1 Pt1-C1 Pt1-C2 C1-N1 C2-C3	3.2198(3) 1.993(10) 2.016(10) 1.156(13) 1.205(14)	Pt1-C1-N1 Pt1-C2-C3 C2-C3-C4 C1-Pt1-C2	178.1(9) 175.6(8) 174.7(10) 90.2(4)	$\begin{array}{c} T \\ \hline \\ \hline \\ P \\ \hline \\ \hline \\ C \\ C$		
			3 ⋅H ₂ 0)		
Pt1-C1 Pt1-C2 C1-N1 C2-C3 Pb1-N1 Pb1-N(pz) Pb1-O1	2.001(9) 1.998(8) 1.150(11) 1.191(11) 2.613(7) 2.446(7)-2.529(6) 2.822(12)	Pt1-C1-N1 Pt1-C2-C3 C2-C3-C4 C1-Pt1-C2	178.4(9) 177.6(8) 177.1(8) 90.0(3)	Pti C1 Pti C2 C3		

Table S3: Emission data for complexes 1-3.						
Complex	Medium (T/K)	$\lambda_{\rm em}/{\rm nm} \ (\lambda_{\rm ex}/{\rm nm})$	$\tau/\mu s ~[\lambda_{em}]$			
1	Solid (298)	452 _{max} , 473 <i>sh</i> (348)	137 [452]			
	Solid (77)	446 _{max} , 467, 481, 493, 518sh (341)	296 [467]			
	CH ₂ Cl ₂ (298)	445 _{max} , 462 <i>sh</i> (345)	a)			
	CH ₂ Cl ₂ (77)	437 _{max} , 459, 469, 481, 501 <i>sh</i> (333)	460 [437]			
2	Solid (298)	$465 \text{s}h^{\text{a}}$, 512, 543 _{max} , 580sh (402)	9 [512], 7 [543]			
	Solid (77)	469, 502 _{max} , 534s <i>h</i> (360)	24 [502]			
3	Solid (298)	448, 501 _{max} , 528sh (361)	33 [448], 18 [501]			
	Solid (77)	450, 471sh, 498, 525sh (365)	52 [450]			

^{a)} Weak emission

		1		2						3			
MO	Pt	C≡CTol	CN	Tl	Pt	C≡CTol	CN	Pb	Pt	C≡CTol	CN	acetone	Тр
L+3	0	100	0	98	0	1	1	10	0	0	0	81	9
L+2	0	100	0	97	0	2	2	11	0	0	0	81	8
L+1	2	98	0	98	0	2	0	66	0	0	1	9	24
LUMO	1	98	1	82	8	5	4	67	0	0	1	8	23
НОМО	41	59	0	0	9	91	0	0	23	77	0	0	0
H-1	21	76	3	0	0	96	4	0	21	78	1	0	0
H-2	97	2	1	2	25	73	0	0	2	96	1	0	0
H-3	57	0	43	0	0	100	0	0	95	3	2	0	0

Table S4: Molecular Orbital Composition in terms of ligands and metals for complexes 1-3.

Table S5: DFT optimized coordinates of $[trans-Pt(C=CTol)_2(CN)_2]^{2-1}$						
Pt	0.00001 -0.00249 0.00016	С	-5.41281 -0.02623 -1.20232			
Ν	0.00022 3.19563 -0.03716	Н	-4.86983 -0.04997 -2.14223			
С	0.00014 2.02389 -0.02338	С	-6.80293 -0.02767 -1.19687			
С	2.01662 -0.00257 -0.00073	Н	-7.3375 -0.05072 -2.14691			
С	3.24977 -0.0022 -0.00123	С	-7.53558 -0.00294 -0.00031			
С	4.66217 -0.00133 -0.00105	С	-6.80513 0.0176 1.19644			
С	5.41304 0.02393 1.20271	С	-5.41404 0.0193 1.20459			
Н	4.87075 0.03986 2.14318	Н	-7.34166 0.03091 2.14548			
С	6.80354 0.02207 1.1965	Н	-4.8732 0.03137 2.14593			
Н	7.33864 0.03917 2.14635	Н	4.87227 -0.06029 -2.14459			
С	7.53557 -0.00357 0.00005	Н	7.34058 -0.06079 -2.14563			
С	6.80452 -0.03356 -1.1966	С	9.04626 0.03432 0.0002			
С	5.41382 -0.03207 -1.20399	Н	9.44108 1.06181 0.00664			
Ν	-0.00021 -3.2006 0.0372	Н	9.46231 -0.46884 0.88159			
С	-0.00013 -2.02886 0.0236	Н	9.46071 -0.45812 -0.88769			
С	-2.01661 -0.00228 0.00137	С	-9.04632 0.03259 -0.00358			
С	-3.24976 -0.00179 0.00214	Η	-9.46486 -0.58108 -0.81113			
С	-4.66216 -0.00087 0.0021	Н	-9.45717 -0.34123 0.94164			
		Н	-9.44253 1.04997 -0.14308			





Figure S1: ${}^{13}C{}^{1}H$ NMR of complex (NBu₄)₂[*trans*-Pt(C=CTol)₂(CN)₂] **1** in

CD₃COCD₃ solution.



Figure S2: (Grey) Absorption spectra of 1 in CH_2Cl_2 (2 × 10⁻⁵ M); Absorption [nm] (10³ $\epsilon/M^{-1}cm^{-1}$): 235(23.3), 264*sh*(30.6), 276(37.2), 318(38.5), 327*sh*(36.0). (Blue) Normalized emission spectra of complex 1 in solid state (up) and CH_2Cl_2 solution (10⁻³ M) (down) at 298 K (solid lines) and 77 K (dotted lines).



Figure S3: Detail of the coordination sphere of Pb^{II} in the molecular structure of **3**.



Figure S4: Emission spectra of complex 2 in solid state at 298 K (solid line) and 77 K

(dotted line).



Figure S5: Frontier orbital plots for 1 obtained by TD-DFT.



Figure S6: Frontier orbital plots for 2 (left) and 3 (right) obtained by TD-DFT.

References:

- 1. I. Collamati and A. Furlani, J. Organomet. Chem., 1969, 17, 457.
- 2. S. Trofimenko, J. Am. Chem Soc., 1967, 89, 3170.
- 3. Gaussian, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. M. Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- (a) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Mater. Phys.*, 1988, **B37**, 785; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 5. W. R. Wadt and P. J. Hay, J. Chem. Phys., 1985, 82, 284.
- 6. Z.Otwinosky and W. Minor, *Methods Enzymol.*, 1997, 276, 307.
- 7. G. M. Sheldrick, *SHELX-97, a program for the refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.
- 8. S. Parkin, B. Moezzi and H. Hope, J. Appl. Crystallogr., 1995, 28, 53.
- 9. R. H. Blessing, Acta Crystallogr. 1995, A51, 33.