Electronic Supplementary Information (ESI)

Aquapentachlororhenate(IV): a singular and promising building block for metal assembling

Donatella Armentano*[a] and José Martínez-Lillo*[b]

[a] *Centro di Eccellenza CEMIF.CAL, Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, via P. Bucci 14/c, 87030, Arcavacata di Rende (CS), Italy. E-mail: donatella.armentano@unical.it*
[b] *Instituto de Ciencia Molecular (ICMol), Universitat de València, C/ Catedrático José Beltrán 2, 46980, Paterna, Valencia, Spain. E-mail: lillo@uv.es.*

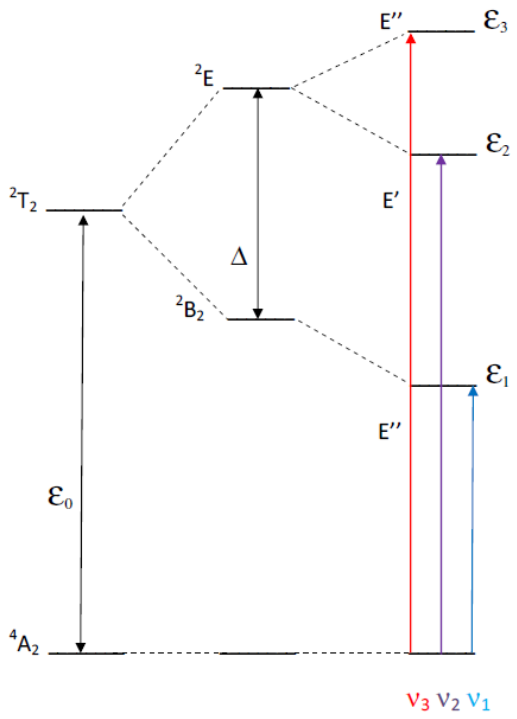
Table of contents. **page**

Preparation of 1.

All manipulations were performed under aerobic conditions, using chemicals as received. Type 3Å molecular sieves were used to dry the MeCN before use, it was not distilled. The $PPh_4[ReCl_5(pyz)]$ precursor was prepared following the literature procedure but by using PPh_4Cl instead of NBu_4Cl (see Ref. 11(a) in the main text).

1. $PPh_4[ReCl_5(pyz)]$ (0.02 mmol, 15.7 mg) was dissolved in acetonitrile (0.1% in H_2O, 3 mL) and added to $MoCl_5$ (0.02 mmol, 5.5 mg) dissolved in ethyl acetate (6 mL). The resulting yellow solution was filtered and left to evaporate at room temperature. Green-yellow crystals of **1** were grown in 2 weeks, which were suitable for X-ray diffraction studies. Yield: 12%. To obtain better yield **1** can be prepared by dissolving $PPh_4[ReCl_5(pyz)]$ in an acetonitrile:water (1:1, v/v, 10 mL) solution and evaporating at room temperature. Yield: 40%. Compound **1** is air-stable over a period of several months without being oxidized under ambient conditions. Anal. Cald. (found) for $C_{24}H_{22}OPCl_5Re$ (**1**): C, 40.0 (39.8); H, 3.1 (2.9) %. IR peaks (cm^{-1}): the absorption associated to water molecule appears at 3450br. **1** is soluble in the majority of the organic solvents, for example, it is soluble in DMF, MeCN and $MeNO_2$.

A)



B) Equation (1):

$$\left.\begin{aligned} \varepsilon_1 &= \lambda/2\,[v + 1/2 - q] \\ \varepsilon_2 &= \lambda\,[v - 1/2] \\ \varepsilon_3 &= \lambda/2\,[(v + 1/2) + q] \end{aligned}\right\} \quad (1)$$

where $q = [v^2 + v + 9/4]^{1/2}$; $\varepsilon_0 = 5P - 17.6 * (B^2/Dq)$; $P = 3B + C \approx 7B$; $C \approx 4B$.

Figure S1. A) Energy levels diagram showing the splitting of the $^2T_2$ term, due to the spin-orbit coupling, and indicating the assignment of the spin-forbidden d-d transitions (ν_1, ν_2 and ν_3) in **1**. B) Expressions employed to calculate the parameters 10Dq, $B_{complex}$, Δ, and λ from the energy values (ε_1 = 13405 cm^{-1}, ε_2 = 14599 cm^{-1}, and ε_3 = 15528 cm^{-1}) of the electronic spectrum of **1** [10Dq = 30000 cm^{-1}, $B_{complex}$ = 435 cm^{-1}, Δ = 970 cm^{-1}, and λ = 1060 cm^{-1}].

Table S1. Selected bond lengths [Å] and angles [°] for **1.**

Re(1)-O(1W)	Re(1)-Cl(1)#2
Re(1)-Cl(1)	Re(1)-Cl(1)#3
Re(1)-Cl(1)#1	Re(1)-Cl(2)
O(1W)-Re(1)-Cl(1)	Cl(1)-Re(1)-Cl(1)#3
O(1W)-Re(1)-Cl(1)#1	Cl(1)#1-Re(1)-Cl(1)#3
Cl(1)-Re(1)-Cl(1)#1	Cl(1)#2-Re(1)-Cl(1)#3
O(1W)-Re(1)-Cl(1)#2	O(1W)-Re(1)-Cl(2)
Cl(1)-Re(1)-Cl(1)#2	Cl(1)-Re(1)-Cl(2)
Cl(1)#1-Re(1)-Cl(1)#2	Cl(1)#1-Re(1)-Cl(2)
O(1W)-Re(1)-Cl(1)#3	Cl(1)#2-Re(1)-Cl(2)
	Cl(1)#3-Re(1)-Cl(2)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+1/2,z

#2 -y+1/2,x,z

#3 -x+1/2,-y+1/2,z

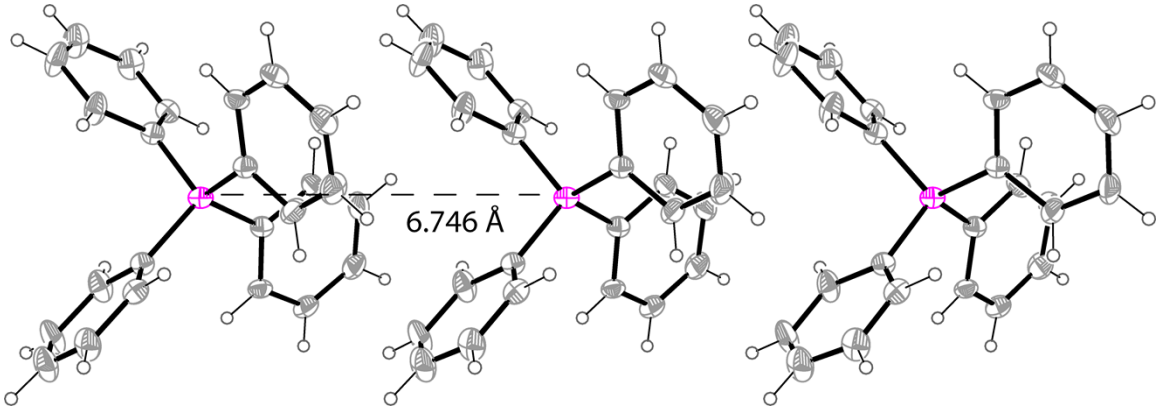


Figure S2. Detail of the *four-fold* phenyl embrace supramolecular motif of the PPh_4^+ cations in **1**, in which four phenyl rings are involved in edge to face intermolecular interactions.

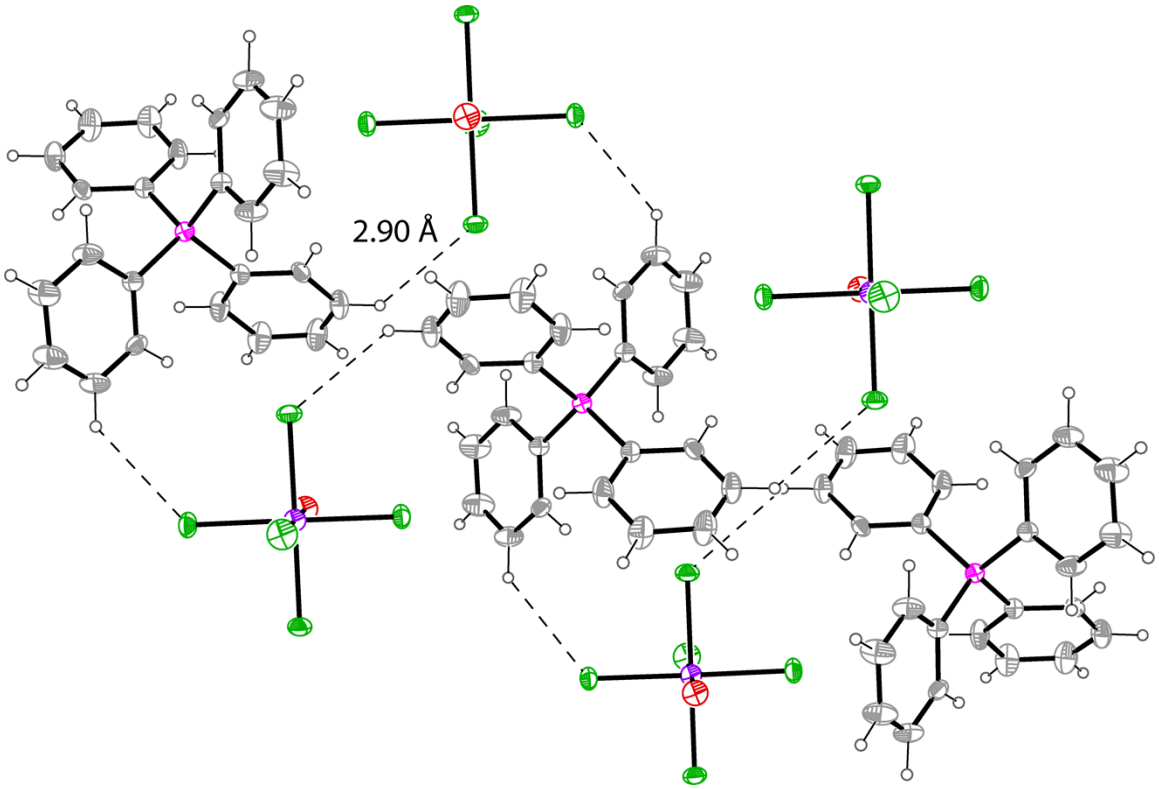


Figure S3. View along the *c* axis of the weak Cl···H-C interactions (dashed lines) between $[ReCl_5(H_2O)]^-$ anions and $(PPh_4)^+$ cations in **1**. Colour code: violet, Re; green, Cl; O, red; pink, P; grey, C; white, H.

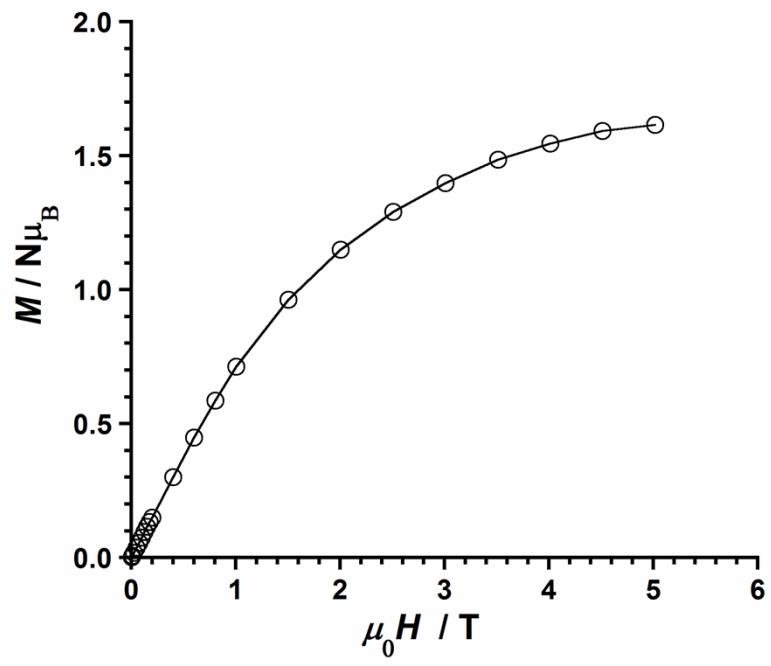


Figure S4. Magnetisation curve for **1** at 2 K. The open circles are the experimental data and the solid line is a visual guide.

$$\hat{H} = D\left[(\hat{S}_Z)^2 - S(S+1)/3\right] + g_{//}\beta H_Z \hat{S}_Z + g_{\perp}\beta (H_X \hat{S}_X + H_Y \hat{S}_Y) \quad (2)$$

$$\chi_M = \frac{\chi_{//} + 2\chi_{\perp}}{3} \quad (3)$$

where

$$\chi_{//} = \frac{N\beta^2 g_{//}^2}{4k(T-\theta)} \frac{1 + 9\exp(-2D/kT)}{1 + \exp(-2D/kT)}$$

$$\chi_{\perp} = \frac{N\beta^2 g_{\perp}^2}{k(T-\theta)} \frac{1 + (3kT/4D)\left[1 - \exp(-2D/kT)\right]}{1 + \exp(-2D/kT)}$$

Figure S5. Hamiltonian [eqn (2)] and its derived analytical expression [eqn (3)] employed to fit the magnetic susceptibility data of compound **1**.

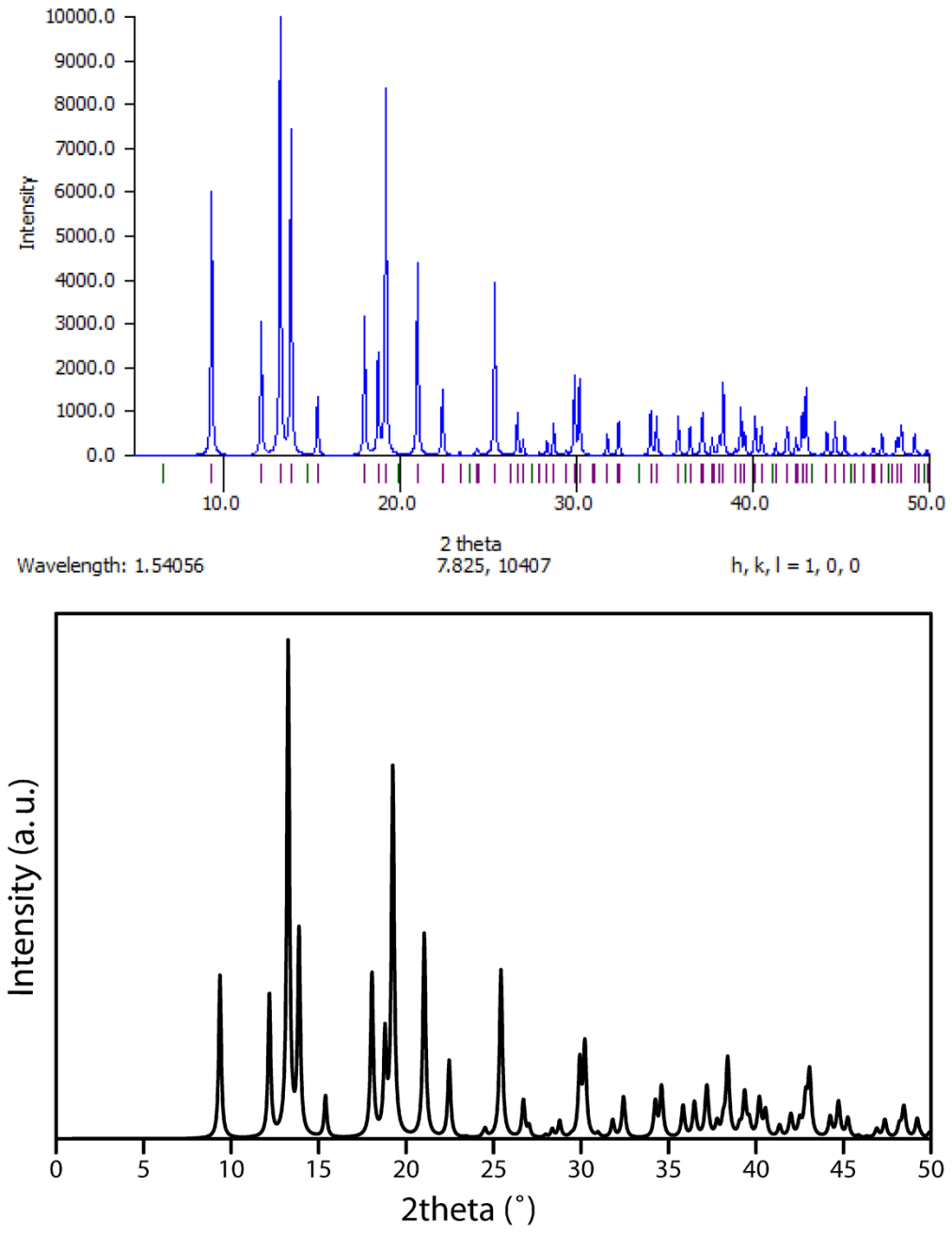


Figure S6. Calculated (top) and experimental (bottom) XRPD pattern profile of **1**, confirming the purity and authenticity of the studied bulk sample.