Electronic Supplementary Information (ESI)

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

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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 PPh₄[ReCl₅(pyz)] precursor was prepared following the literature procedure but by using PPh₄Cl instead of NBu₄Cl (see Ref. 11(a) in the main text).

1. PPh₄[ReCl₅(pyz)] (0.02 mmol, 15.7 mg) was dissolved in acetonitrile (0.1% in H₂O, 3 mL) and added to MoCl₅ (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 PPh₄[ReCl₅(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 C₂₄H₂₂OPCl₅Re (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 MeNO₂.
A)

\[ \begin{align*}
\varepsilon_1 &= \frac{\lambda}{2} [v + 1/2 - q] \\
\varepsilon_2 &= \lambda [v - 1/2] \\
\varepsilon_3 &= \frac{\lambda}{2} [(v + 1/2) + q]
\end{align*} \] (1)

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

**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 (\( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \)) in 1. B) Expressions employed to calculate the parameters 10Dq, \( B_{\text{complex}} \), \( \Delta \), and \( \lambda \) from the energy values (\( \varepsilon_1 = 13405 \text{ cm}^{-1}, \varepsilon_2 = 14599 \text{ cm}^{-1}, \) and \( \varepsilon_3 = 15528 \text{ cm}^{-1} \)) of the electronic spectrum of 1 [10Dq = 30000 cm\(^{-1}\), \( B_{\text{complex}} = 435 \text{ cm}^{-1}, \Delta = 970 \text{ cm}^{-1}, \) and \( \lambda = 1060 \text{ cm}^{-1} \)].
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<td>Symmetry Transformations</td>
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#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 PPh₄⁺ 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 [ReCl₃(H₂O)]⁺ anions and (PPh₄)⁺ 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.
\[ \hat{H} = D \left( \hat{S}_Z^2 - \frac{S(S+1)}{3} \right) + g_\parallel \beta H_Z \hat{S}_Z + g_\perp \beta (H_X \hat{S}_X + H_Y \hat{S}_Y) \] (2)

\[ \chi_M = \frac{\chi_\parallel + 2 \chi_\perp}{3} \] (3)

where

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

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

**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.