Electronic supplementary information (ESI)

Synthesis, crystal structure and magnetic properties of the complex [ReCl$_3$(tppz)] · MeCN

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Table S1. Selected magneto-structural data for six-coordinate rhenium(III) complexes$^a$

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$^a$ Only six-coordinate Re(III) complexes with a ReN3Cl3 chromophore were considered.

$^b$ Abbreviation for the ligands: py = pyridine, Hpz = pyrazole, 3,5-lut = 3,5-dimethylpyridine, L1Et = (2-C5H4NCH2)2NCH2CO2C2H5, L4Et = (2-C5H4NCH2)N(CH3C3H2N2CH2)(CH2CO2C2H5).

$^c$ Not measured.
Figure S1. IR spectrum of 1.

Figure S2. X-ray powder diffraction pattern of 1: (black) experimental; (red) simulation of the powder pattern from the crystal structure.
Figure S3. $^1$H (a) and $^{13}$C NMR (b) spectra of compound 1.
Appendix: Energy levels for a $^{3}T_{1}$ term arising from the $t_{2}^{4}$ electronic configuration under a tetragonal ligand-field and spin-orbit coupling

In order to simplify the calculations, we take advantage of the isomorphism between the orbital triplet $^{3}T_{1}$ coming from the $t_{2}^{4}$ electronic configuration and the triplet $L = 1$ from a $^{3}P$ term ($p^{4}$ electronic configuration). The matrix elements of $L$ within the orbital triplet $T_{1}$ are exactly the same than those contained in the matrix of $(-1)L$ in the associated $P$ state (strong ligand-field approach). So, we can use the $|T_{1}| = -\kappa|P|$ relationship where $\kappa$ is the orbital reduction factor due to the covalency effects.\(^{19}\) In this respect, the wave-functions for the $^{3}T_{1}$ term are written in the form of $|M_{L}, M_{S}\rangle$ with $M_{L} = 0, \pm 1$ and $M_{S} = 0, \pm 1$. The tetragonal distortion and spin-orbit coupling are treated simultaneously through the Hamiltonian of eqn (1)

$$\hat{H} = -\kappa\lambda \hat{L} \hat{S} + \Delta (\hat{L}_{z}^{2} - 2/3)$$  \hspace{1cm} (1)

where the first term is the spin-orbit coupling, the second one accounts for the orbital distortion of the triplet $T_{1}$ [$T_{1}$ breaks its degeneracy under a $C_{4}$ symmetry group giving an orbital doublet ($E$) and an orbital singlet ($A_{2}$) which are separated by an energy gap ($\Delta$)]. $\kappa$ is the orbital reduction due to covalency.

The secular determinant relevant to the application of the Hamiltonian of eqn (1) may be arranged and factorized in the following sub-determinants:\(^{19}\)

\[
\begin{array}{|c|c|c|}
\hline
& |1, -1\rangle & |-1, 1\rangle \\
\hline
<1, -1| & (\Delta/3\kappa\lambda)\lambda & -\kappa\lambda \\
\hline
<-1, 1| & 0 & (\Delta/3\kappa\lambda)\lambda \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|}
\hline
& |1, 1\rangle & |0, 0\rangle & |-1, -1\rangle \\
\hline
<1, 1| & (\Delta/3\kappa\lambda)\lambda & -\kappa\lambda & 0 \\
\hline
<0, 0| & -\kappa\lambda & -2\Delta/3 - E & -\kappa\lambda \\
\hline
<-1, -1| & 0 & -\kappa\lambda & (\Delta/3\kappa\lambda)\lambda \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|}
\hline
& |1, 0\rangle & |0, -1\rangle & |-1, 0\rangle & |0, 1\rangle \\
\hline
<1, 0| & \Delta/3 - E & -\kappa\lambda & 0 & 0 \\
\hline
\end{array}
\]
The values of the energy levels from these determinants are:

\[ E_1 = E_2 = \frac{\Lambda}{3} - \kappa \lambda \]

\[ E_3 = E_4 = \frac{1}{2} \left[ -\frac{\Lambda}{3} + \left( \Delta^2 + 4\kappa^2 \lambda^2 \right)^{1/2} \right] \]

\[ E_5 = E_6 = \frac{1}{2} \left[ -\frac{\Lambda}{3} - \left( \Delta^2 + 4\kappa^2 \lambda^2 \right)^{1/2} \right] \]

\[ E_7 = \frac{\Lambda}{3} + \kappa \lambda \]

\[ E_8 = \frac{1}{2} \left[ -\frac{\Lambda}{3} + \kappa \lambda + \left( \Delta^2 + 2\kappa \lambda \Delta + 4\kappa^2 \lambda^2 \right)^{1/2} \right] \]

\[ E_9 = \frac{1}{2} \left[ -\frac{\Lambda}{3} + \kappa \lambda - \left( \Delta^2 + 2\kappa \lambda \Delta + 4\kappa^2 \lambda^2 \right)^{1/2} \right] \]