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Electronic supplementary information (ESI)

Synthesis, crystal structure and magnetic properties of the complex $[ReCl_3(tppz)] \cdot MeCN$

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

$[ReX_3L_3]$[b]	Re–X	Re–N	Configuration of halide anions	Magnetic properties	Ref.
$[ReCl_3(py)_3]$	2.367(2) 2.367(2) 2.397(2)	2.117(8) 2.120(8) 2.116(5)	*mer*	c	14b
$[ReBr_3(py)_3]$	2.513(2) 2.506(2) 2.534(2)	2.111(10) 2.122(10) 2.121(9)	*mer*	c	14b
$[ReCl_3(Hpz)_3]$	2.3220(18) 2.3101(18) 2.3120(18)	2.133(5) 2.095(5) 2.093(5)	*mer*	1.8 BM	14j
$[ReCl_3(3,5\text{-lut})_3]$	2.356(4) 2.3624) 2.402(4)	2.13(1) 2.13(1) 2.12(1)	*mer*	c	14d
$[ReCl_3(L^1Et)]$	2.384(3) 2.384(3) 2.391(4)	2.075(9) 2.075(9) 2.154(14)	*fac*	paramegnetic	14h
$[ReCl_3(L^4Et)]$	2.3741(17) 2.3996(16) 2.4040(17)	2.078(6) 2.084(5) 2.209(5)	*fac*	c	14h

[a] Only six-coordinate Re(III) complexes with a ReN_3Cl_3 chromophore were considered.
[b]Abbreviation for the ligands: py = pyridine, Hpz = pyrazole, 3,5-lut = 3,5-dimethylpyridine, L^1Et = $(2\text{-}C_5H_4NCH_2)_2NCH_2CO_2C_2H_5$, L^4Et = $(2\text{-}C_5H_4NCH_2)N(CH_3C_3H_2N_2CH_2)(CH_2CO_2C_2H_5)$.
[c] Not measured.

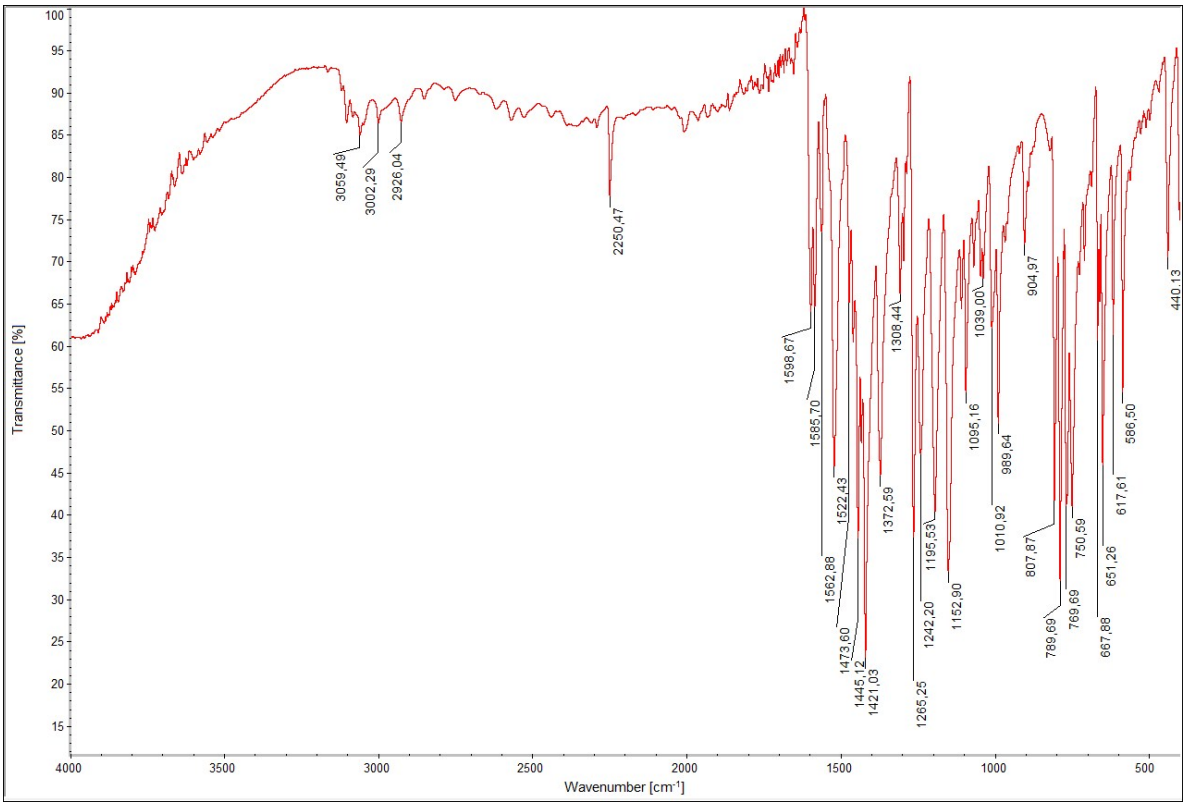


Figure S1. IR spectrum of **1**.

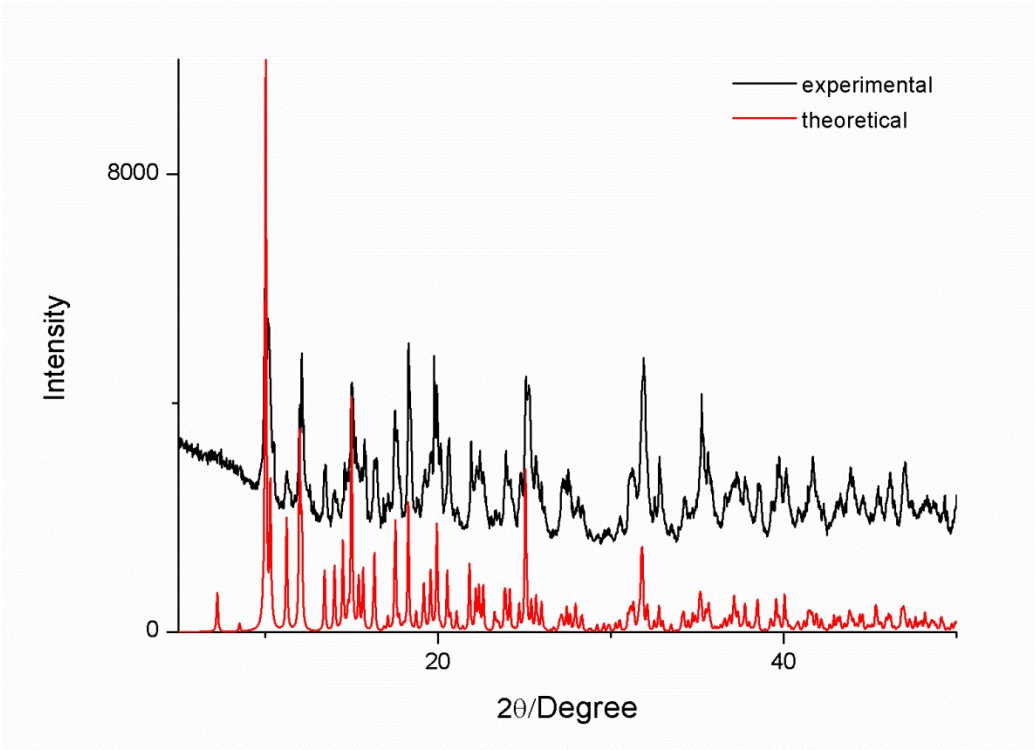
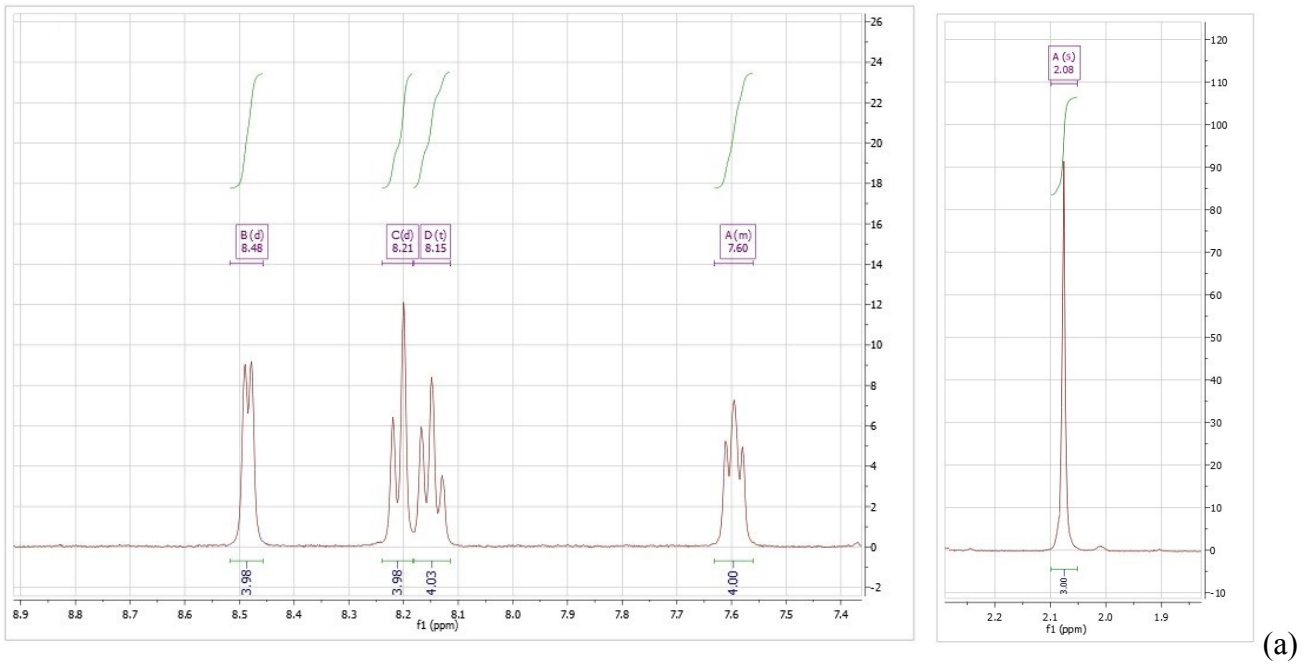
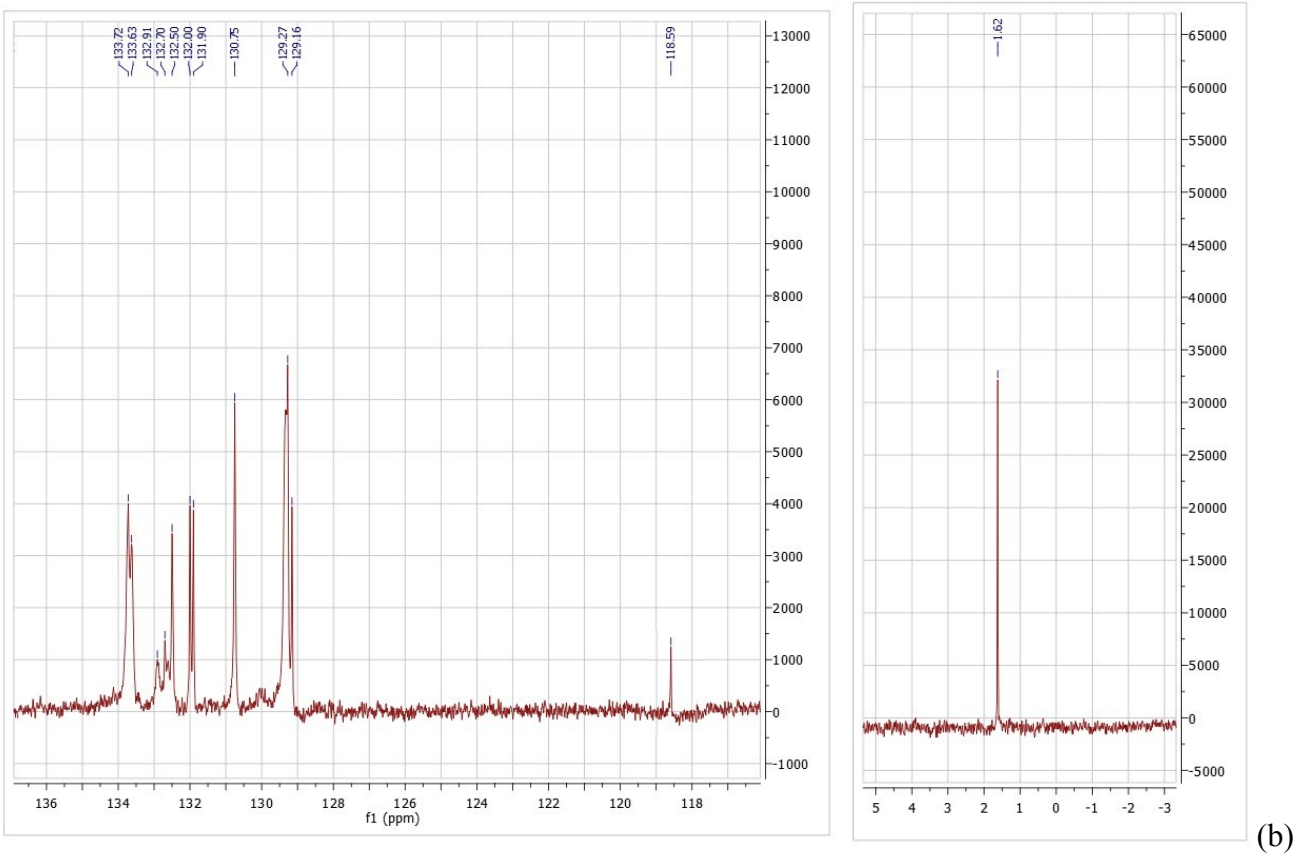


Figure S2. X-ray powder diffraction pattern of **1**: (black) experimental; (red) simulation of the powder pattern from the crystal structure.



(a)



(b)

Figure S3. ^{1}H (a) and ^{13}C NMR (b) spectra of compound **1**.

Appendix: ***Energy levels for a $^3T_1$ 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 $^3T_1$ coming from the t_2^4 electronic configuration and the triplet L = 1 from a ^3P term (p^4 electronic configuration). The matrix elements of $\boldsymbol{L}$ within the orbital triplet T_1 are exactly the same than those contained in the matrix of (-1)$\boldsymbol{L}$ in the associated P state (strong ligand-field approach). So, we can use the $||\boldsymbol{T_1}|| = -\kappa\,||\boldsymbol{P}||$ relationship where κ is the orbital reduction factor due to the covalency effects.[19] In this respect, the wave-functions for the $^3T_1$ term are written in the form of $|M_L, M_S\rangle$ with M_L = 0, ±1 and M_S = 0, ±1. The tetragonal distortion and spin-orbit coupling are treated simultaneously through the Hamiltonian of eqn (1)

$$\hat{H} = -\kappa\lambda\hat{L}\hat{S} + \Delta(\hat{L}_z^2 - 2/3) \qquad (1)$$

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 (Δ)]. κ 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]

	|1, -1>	|-1, 1>
<1, -1|	(Δ/3-$\kappa\lambda$)-E	0
<-1, 1|	0	(Δ/3-$\kappa\lambda$)-E

	|1, 1>	|0, 0>	|-1, -1>
<1, 1|	(Δ/3+$\kappa\lambda$)-E	-$\kappa\lambda$	0
<0, 0|	-$\kappa\lambda$	-2Δ/3- E	-$\kappa\lambda$
<-1, -1|	0	-$\kappa\lambda$	(Δ/3+$\kappa\lambda$)-E

	|1, 0>	|0, -1>	|-1, 0>	|0, 1>
<1, 0|	Δ/3-E	-$\kappa\lambda$	0	0

<0, -1|	$-\kappa\lambda$	$-2\Delta/3- E$	0	0
<-1, 0|	0	0	$\Delta/3-E$	$-\kappa\lambda$
<0, 1|	0	0	$-\kappa\lambda$	$-2\Delta/3-E$

The values of the energy levels from these determinants are:

$$E_1 = E_2 = \frac{\Delta}{3} - \kappa\lambda$$

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

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

$$E_7 = \frac{\Delta}{3} + \kappa\lambda$$

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

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