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

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The reaction of the starting materials [Re^{III}Cl$_3$(MeCN)(PPh$_3$)$_2$] or [Re^{V}OCl$_3$(PPh$_3$)$_2$] with 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) in acetonitrile yielded the Re(III) complex [ReCl$_3$(tppz)]$^.$MeCN (**1**). This complex crystallizes in the monoclinic space group P2$_1$/n and its crystal structure consists of neutral mononuclear entities with a meridional geometry of the chloride ligands, the six-coordination of the Re(III) ion being completed by the tridentate tppz ligand. Each metal centre exhibits a highly distorted octahedral coordination with Re−Cl and Re−N$_{tppz}$ bond lengths covering the ranges 2.3590(9)-2.3606(8) and 1.971(2)-2.096(2) Å, respectively. The magnetic properties of **1** have been investigated in the temperature range 1.9-290 K. They are charateristic of a six-coordinate Re(III) mononuclear complex with d^4 low-spin (^{3}T$_1$ ground state). The magnetic data of **1** are discussed through a deep analysis of the influence of the ligand-field, spin-orbit coupling, tetragonal distortion and covalency effects. The second-order Zeeman effect between the the non-magnetic ground state (M_J = 0) and higher energy levels ($M_J \neq 0$) determine magnetic susceptibility of **1**, the value of the temperature-independent paramagnetic susceptibiity being 3378 x 10^{-6} cm^3 mol^{-1}. This value compares well with those reported for other structurally characterized Re(III) complexes.

Introduction

2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz), synthesized by Goodwin and Lions in 1959[1], is a remarkably versatile high-electron donor ligand offering a wide variety of binding modes for construction of novel systems. It has evidenced that tppz can act as bidentate (α, β and γ), tridentate, bis-bidentate, tris-bidentate and bis-tridentate ligand[2] as well as a counterion in its deprotonated form.[3] Up to now, 206 compounds incorporating tppz have been reported. Among them, 59 complexes are mononuclear and 147 are multinuclear (including bi-, tri-, tetranuclear compounds).[4]

A scientific interest in tppz complexes can be attributed to rich photophysical and redox properties associated with these compounds making them useful for analytical purposes and probes for biologically relevant molecules such as DNA.[5] More recently, tppz has been examined as fluorescence sensors for series of metal ions and off-off-on switching of fluorescence depending on stepwise complex formation with tppz has been reported.[6] A particular emphasis has been paid to studies of the homo- and hetero-polynuclear ruthenium complexes

which have shown that tppz is an effective mediator for intermetallic coupling nearly of the order of the Creuze-Taube ion.[6]

Another relevant aspect of the coordination chemistry of tppz concerns the ability of this polydentate organic ligand as a bridge to mediate magnetic interactions between paramagnetic centers separated by more than 6.4 Å. The compounds incorporating the unit [M$_2$(tppz)]$^{4+}$ [M = Ni(II) and Cu(II)] were found to exhibit significant antiferromagnetic interactions between the paramagnetic metal ions involved.[2b,8] Interestingly, the relatively good efficiency of the tppz bridge in transmitting magnetic interactions between paramagnetic centers contrasts with the much poorer ability of the related bridging pyrazine molecule in its metal complexes, where negligible or weak antiferromagnetic interactions were observed (J values ranging from -7.4 to 0 cm^{-1}).[9] Finally, mononuclear complexes of Co(II) of formula [Co(tppz)$_2$]$^{2+}$ with the tppz ligands coordinated in a tridentate coordination mode deserve to be mentioned. These compounds attract scientific interest due to the thermally induced spin crossover behavior from a high-spin S$_{Co}$ = 3/2 at high temperatures to a low-spin S$_{Co}$ = 1/2 at lower temperatures.[2b,8b,10]

The present contribution covers the synthesis and magneto-structural characterization of the new mononuclear rhenium(III) complex [ReCl$_3$(tppz)]$^.$MeCN (**1**). The coordination chemistry of Re(III) is dominated by the diamagnetic Re$_2$$^{6+}$ core.[11] Examples of mononuclear Re(III) complexes incorporating phosphorus,[12] sulphur[13] and less frequently nitrogen[14] or oxygen[15] donor ligands have also been described but their magnetic behavior, with compounds exhibiting

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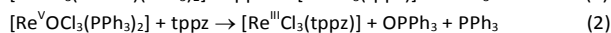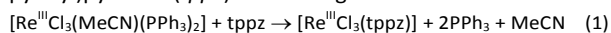
different degrees of paramagnetism and even diamagnetism,[14h,m,15d] can still be considered as largely unexplored.

Results and Discussion

Synthesis

The complex [ReCl$_3$(tppz)]·MeCN (**1**) was prepared by treating [ReOCl$_3$(PPh$_3$)$_2$] or [ReCl$_3$(MeCN)(PPh$_3$)$_2$] with 2,3,5,6-tetra-(2-pyridyl)pyrazine (*tppz*) in refluxing acetonitrile:

[Re^{III}Cl$_3$(MeCN)(PPh$_3$)$_2$] + tppz → [Re^{III}Cl$_3$(tppz)] + 2PPh$_3$ + MeCN   (1)

[Re^{V}OCl$_3$(PPh$_3$)$_2$] + tppz → [Re^{III}Cl$_3$(tppz)] + OPPh$_3$ + PPh$_3$ (2)

A relatively high yield of [ReCl$_3$(tppz)] (ca. 70%) in the reaction (2) indicates that the tridentate nitrogen donor *tppz* facilitates the substitution of the phosphine ligands and then the abstraction of the oxo group and reduction to the [Re^{III}Cl$_3$] unit. A similar trend was confirmed by Zubieta *et al*. for bifunctional chelators based on pyridyl, imidazole- and carboxylate-derivatized amino acids.[14f] In general, the use of additional PPh$_3$ is necessary to abstract the oxo group and reduce the [Re^V=O]$^{3+}$ core of the [ReOCl$_3$(PPh$_3$)$_2$] complex to the [Re^{III}Cl$_3$] unit.[14m,16]

Crystal Structure

Compound **1** crystallizes in the monoclinic space group *P*2$_1$/*n* (Table 1) and its crystal structure consists of neutral [ReCl$_3$(tppz)] units and solvated acetonitrile molecules. A perspective view of the asymmetric unit of **1** together with the atom numbering is shown in Figure 1. No intermolecular interactions with enough strength to govern crystal packing or molecule conformation were found in the structure of **1** except for weak intra- and intermolecular C—H•••N and C—H•••Cl type interactions [C(6)—H(6)•••N(4) with D•••A distance = 2.570 Å and D—H•••A angle = 114.0°, C(6)—H(6)•••Cl(1)^a with D•••A distance = 2.760 Å and D—H•••A angle = 139.0° and C(22)—H(22)•••N(99)^b with D•••A distance = 2.560 Å and D—H•••A angle = 134.0°; symmetry code: (a) = -*x*,1-*y*,-*z*] and (b) = 1-*x*,2-*y*,-*z*] and Re—Cl•••π contacts [Re1–Cl1•••Cg1^a(N4–C10–C11–C12–C13–C14) with a distance of 3.761(2) Å and an angle (between X(I)→Cg(J) vector and normal to plane J) of 10.99°] (Figure 2).

The Re(III) ion is six-coordinate in a highly distorted octahedral geometry defined by three nitrogen atoms of the tridentate coordinated *tppz* ligand and three chloride donors, *meridionally* arranged. The major angular distortions from the idealized octahedral geometry, reflected in the *cisoid* [77.45(9)–103.44(7)°] and *transoid* [154.98(10)–179.08(7)°] angles, are attributed to geometrical constraints issued from the occurrence of two fused five-member chelate rings of the tridentate *tppz* ligand, resulting in N(2)–Re(1)–N(1) and N(2)–Re(1)–N(3) angles of 77.45(9) and 77.58(9)°, respectively (Table 2). The *tppz* molecule as a whole is far from planarity.

The dihedral angles between the mean planes of the two coordinated pyridyl rings and the pyrazine ring are 12.41(14) and 22.41(11)°, while the uncoordinated pyridyl rings are inclined to the pyrazine ring by 67.46(8) and 38.25(12)°. Low energy conformations of the free *tppz* are predicted to have each pyridyl ring twisted from coplanarity with the pyrazine by roughly 50°.[2f]

The Re–Cl distances [2.3606(8), 2.3590(9) and 2.3597(8) Å] compare well with the values reported for the related Re(III) complexes with the six-coordinate metal centre in a distorted ReN$_3$Cl$_3$ octahedral geometry (Table S1). The bond length of Re(III) to the middle tppz-nitrogen atom N(2) [1.971(2) Å] is shorter than the Re(1)–N(1) and Re(1)–N(3) distances [2.084(2) and 2.096(2) Å], a pattern which is usually observed in complexes incorporating *tppz*-like ligands.[14a,17] The shortness of Re–N$_{pyrazine}$ distance within the *tppz* unit is attributed to a more efficient overlap of the t$_{2g}$ metal orbitals with the π* orbitals of the central pyrazine ring compared to the distal pyridyl groups.

Table 1. Crystal data and structure refinement for complex **1**

	1
Empirical formula	C$_{26}$H$_{19}$Cl$_3$N$_7$Re
Formula weight (g mol^{-1})	722.03
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*P*2$_1$/*n*
Unit cell dimensions (Å,°)	*a* = 14.9278(4)
	b = 10.2675(2)
	c = 17.3725(5)
	β = 99.442(3)
Volume (Å^3)	2626.63(12)
Z	4
ρ$_{calcd}$ (Mg m^{-3})	1.826
Absorption coefficient (mm^{-1})	4.962
F(000)	1400
Crystal size [mm]	0.051x0.088 x 0.104
ϑ range for data collection [°]	3.34 to 25.05
Index ranges	-17 ≤ *h* ≤ 17
	-12 ≤ *k* ≤ 12
	-20 ≤ *l* ≤ 20
Reflections collected	14243
Independent reflections	4633 [*R*$_{int}$ = 0.0296]
Completeness to 2ϑ = 25°	99.8%
Min. and max. transm.	0.617 and 1.000
Data/restraints/parameters	4633 / 0 / 335
R indices (all data)	*R*$_1$ = 0.0272
	w*R*$_2$ = 0.0453
Largest diff. peak and hole (e Å^{-3})	0.560 and -0.375

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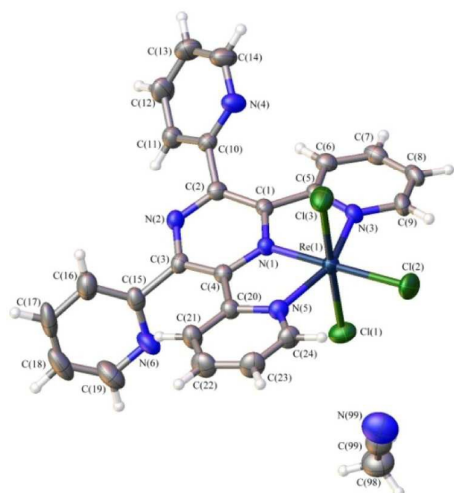**Figure 1.** Perspective view of the molecular structure of [ReCl₃(tppz)]·MeCN (**1**) showing the atom numbering. Displacement ellipsoids are drawn at 50% probability level.
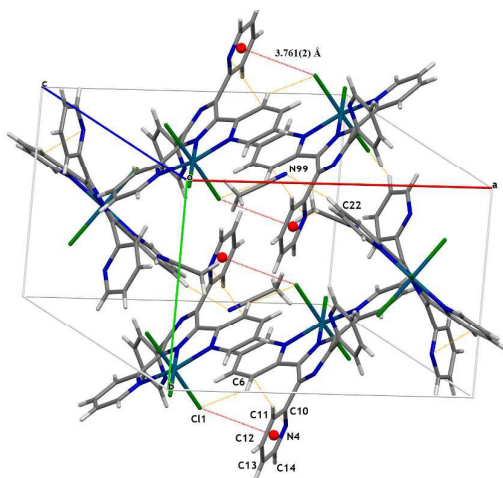

Figure 2. View of the molecular packing of **1** with marked Re—Cl•••π as well as C—H•••N and C—H•••Cl type interactions.

Table 2. The selected bond lengths (Å) and angles (°) for **1**

Bond lengths		Bond angles	
Re(1)–N(1)	1.971(2)	N(1)–Re(1)–N(3)	77.58(9)
Re(1)–N(3)	2.096(2)	N(1)–Re(1)–N(5)	77.45(9)
Re(1)–N(5)	2.084(2)	N(1)–Re(1)–Cl(1)	91.44(7)
Re(1)–Cl(1)	2.3606(8)	N(1)–Re(1)–Cl(2)	179.08(7)
Re(1)–Cl(2)	2.3590(9)	N(1)–Re(1)–Cl(3)	90.93(7)
Re(1)–Cl(3)	2.3597(8)	N(3)–Re(1)–Cl(1)	90.69(7)
		N(3)–Re(1)–Cl(2)	101.53(7)
		N(3)–Re(1)–Cl(3)	90.97(7)
		N(5)–Re(1)–N(3)	154.98(10)
		N(5)–Re(1)–Cl(1)	88.19(7)
		N(5)–Re(1)–Cl(2)	103.44(7)
		N(5)–Re(1)–Cl(3)	91.17(7)
		Cl(2)–Re(1)–Cl(1)	88.82(3)
		Cl(2)–Re(1)–Cl(3)	88.83(3)
		Cl(3)–Re(1)–Cl(1)	177.36(3)

Magnetic properties

It is well known that that the octahedral ligand field for 5d metal ions is always strong and so the d⁴ electronic configuration of the six-coordinate Re(III) ion is defined by a low-spin state $^3T_1$ term (t_2^4), which, in the case of **1** is split by the spin–orbit coupling (SOC) and an axial ligand field as shown in Figure 3 (hereafter the symbol of the parity will be omitted). SOC splits the $^3T_1$ term into three spin-orbit energy levels ($J = 0$, 1 and 2, as shown in the central part of Figure 3), being the non-magnetic singlet, $J = 0$, the ground state for $\lambda < 0$ (λ is the spin–orbit coupling parameter). In the absence of SOC, a tetragonal distortion splits the $^3T_1$ term into an orbital singlet ($^3A_2$) and an orbital doublet (^2E) separated by an energy gap (Δ) which is defined as positive if the orbital singlet is the lowest (left of Fig. 3) or negative in the reverse situation (right of Fig. 3). Due to the strong spin–orbit coupling and ligand-field acting in the 5d metal ions, both perturbations have to be taken into account simultaneously.
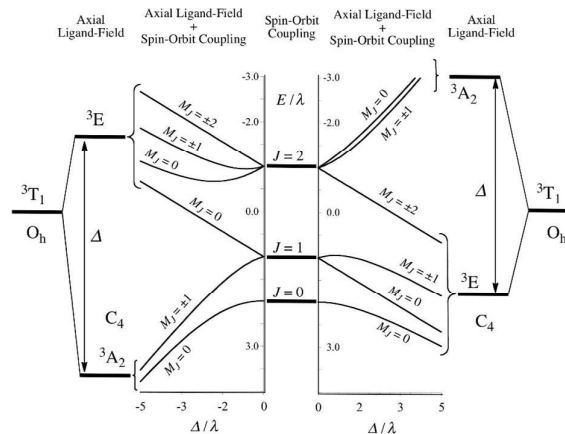

Figure 3. Splitting of the $^3T_1$ term of the t_2^4 electronic configuration by spin-orbit coupling and a tetragonal ligand-field component.

Having these considerations in mind and in order to interpret the magnetic properties of **1**, we used the Hamiltonian of eqn (3) (see Appendix)

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

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 giving an orbital doublet E and anorbital singlet A_2 under a C_4 symmetry group, which are separated by an energy gap Δ). κ is the orbital reduction due to covalency.

In the case of a strict octahedral symmetry (Δ = 0), an exact analytical equation for the magnetic susceptibility can be deduced [eqn (4)].

$$\chi_M = \frac{N\beta^2}{2\lambda}\left[\frac{-(8/3\kappa)(2+\kappa)^2 + (x+9)\exp(x) + (5x+15)\exp(3x)}{1+3\exp(x)+5\exp(3x)}\right] \quad (4)$$

where $x = \lambda/kT$.[18] When a lower symmetry is present, the dependence of the susceptibility on temperature is complicated and no analytical expression can be obtained. As shown in Figure 3, nine non-degenerate energy levels appear ($|J,M_J\geq$ functions) under a tetragonal ligand-field distortion. The relevant determinants and the energy values for each level are given in the Appendix.[19] These levels are plotted in Figure 3 as a function of the Δ/λ ratio.

From Figure 3 and for $\lambda < 0$, one can see that the singlet $M_J = 0$ is always the ground state for any value of Δ (positive or negative) and also that the energy gap between this non-magnetic ground state and the first magnetic excited state ($M_J = \pm 1$) is of the same order as $|\lambda|$. Due to the strong SOC ($\lambda \approx -1250$ cm^{-1}),[18] one can assume that the ground state is the only populated one at room temperature and below ($kT < \lambda$). Therefore, the magnetic susceptibility for **1** arises only from the second-order Zeeman effect between the non-magnetic ground state ($M_J = 0$) and higher magnetic levels ($M_J \neq 0$), that is, a temperature-independent paramagnetic susceptibility (χ_{TIP}). In this respect, from eqn (4) and for $|\lambda|/kT \gg 1$, one obtains eqn (5):

$$\chi_M \approx \chi_{TIP} = \frac{4N\beta^2(2+\kappa)^2}{3\kappa|\lambda|} \quad (5)$$

Then, the experimental thermal dependence of the $\chi_M T$ product of **1** below room temperature is expected to follow a straight line which tends to zero when the temperature vanishes ($\chi_M T = $ constant value $\times T$).

Figure 4 shows a family of $\chi_M T$ curves as a function of temperature for different values of the λ, Δ and κ parameters. These curves are obtained through the Hamiltonian of eqn (3) and using the VPMAG program.[20] In all these curves, one can see that the $\chi_M T$ values tend linearly to zero at low temperatures. It is interesting to note that ligand fields of low symmetry whose values are of the same order of magnitude as (or less than) the spin-orbit coupling constant ($|\Delta| \leq |\lambda|$) do not much affect the average paramagnetism of the t_2^4 configuration, so that one may largely neglect them in dealing with regular octahedral complexes and use eqn (5) to evaluate the temperature independent paramagnetism. So, if we assume the free-ion parameter $\lambda_0 \approx 1250$ cm^{-1} and an orbital reduction parameter $\kappa \approx 0.75$ (value commonly observed for 5d metal ions),[18,21] a value of the χ_{TIP} about 3000×10^{-6} cm^3 mol^{-1} for six-coordinate Re(III) complexes can be expected.

The $\chi_M T$ versus T plot for **1** (χ_M is the magnetic susceptibility per mol of Re(III) ions] is shown in Figure 5. A linear plot is observed, as expected. At room temperature, $\chi_M T$ is equal to 0.93 cm^3 mol^{-1} K and it decreases linearly with temperature, as predicted.
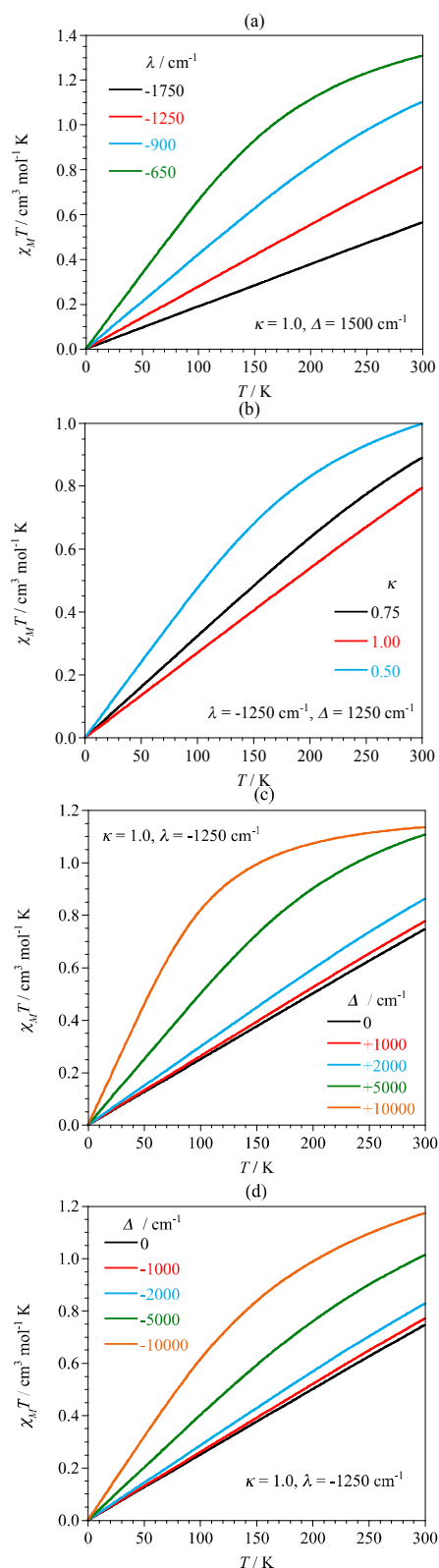

Figure 4. Theoretical $\chi_M T$ vs. T plots as a function of (a) the spin-orbit parameter (λ), (b) reduction parameter (κ), (c), positive tetragonal field ($\Delta > 0$) and (d) negative tetragonal field ($\Delta < 0$).

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However, it does not tend to zero when temperature vanishes, but to *ca* 0.010 cm^3 mol^{-1} K. This feature may be attributed to the presence of some paramagnetic impurity, most likely due to an oxidation of a very small amount of Re(III) to Re(IV). A satisfactory match of the experimental $\chi_M T$ values is achieved through eqn (3) with the introduction of a paramagnetic impurity (ρ) in the form of eqn (6).

$$\chi T_{exp} = (1 - \rho) \chi T_{Re(III)} + \rho \chi T_{Re(IV)} \qquad (6)$$

where $\chi T_{Re(IV)} = \dfrac{N\beta^2 g^2}{3k} S(S+1) \approx 1.60$ cm^3 mol^{-1} K (for $S = 3/2$ and $g = 1.85$).

Least-squares best-fit parameters through the VPMAG program[20] were: λ = -1190(20) cm^{-1}, Δ = 1010(25) cm^{-1}, κ = 0.720(5) and ρ = 0.00625(2) [that is *ca*. 0.63% of Re(IV) is present in **1**]. The corresponding value of the χ_{TIP} is 3080 × 10^{-6} cm^3 mol^{-1}. This value is very close to that calculated by eqn (5) and it is also similar to those observed in other Re(III) complexes.[18,22] However, in the temperature range explored (1.9-290 K), all these parameters (λ, Δ and κ) are very correlated and it is not possible to obtain unambiguous values for them. Even, the sign for Δ cannot be unambiguously determined. The values of the parameters given above are one of the more reliable set of the best fits. Moreover, because of the large correlation existing between diamagnetism of the ligands (χ_{dia}) and the χ_{TIP}, the experimental magnetic susceptibilities obtained for **1** were carefully corrected for the diamagnetism of the constituent atoms [χ_{dia} = −397 × 10^{-6} cm^3 mol^{-1}] and also for the sample holder.
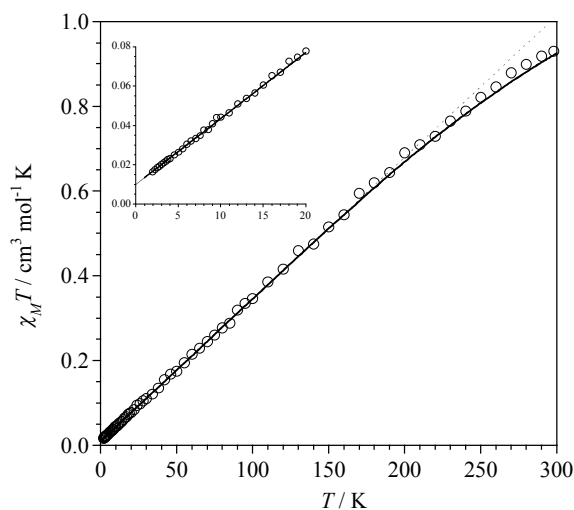

Figure 5. Temperature dependence of the $\chi_M T$ product for **1**: (o) experimental); (—) theoretical curve through Hamiltonian of eqn (3) and the best-fit parameters (see text) ; (---) linear fit from equation $\chi_M T = A + BT$ (see text). The inset shows a detail of the low temperature domain.

Finally, it is interesting to note that, for this type of Re(III) complexes, which have large values of λ (λ >> kT), the experimental thermal dependence of the $\chi_M T$ product is expected to follow a straight line, $\chi_M T = A + BT$, where A is the value of $\chi_M T$ corresponding to the occurrence of a small paramagnetic impurity and B is the temperature-independent paramagnetism (χ_{TIP}) of Re(III) defined by eqn (5) (the octahedral distortion Δ being neglected). In the case of **1**, a fit to a linear plot yields A = 0.00998 cm^3 mol^{-1} K [which corresponds to 0.63% of Re(IV) in **1**] and B = 0.003110 cm^3 mol^{-1} (χ_{TIP} = 3110 × 10^{-6} cm^3 mol^{-1}). These values are practically the same than those obtained through eqn (3).

Conclusions

The preparative routes of complex **1** whose crystal structure and magnetic properties are described herein demostrate that tridentate nitrogen donors such as *tppz* make easy the substitution of the phosphine ligands and the release of the oxo group with reduction of the [Re^V=O]$^{3+}$ core from the [ReOCl$_3$(PPh$_3$)$_2$] complex to the [ReCl$_3$] entity. A deep analysis of the variable-temperature magnetic data of **1** reveals that it is a d^4 low-spin species (^{3}T$_1$ ground state) whose magnetic behaviour is dictated by a large spin-orbit coupling [λ = -1190(20) cm^{-1}]. Therefore, the magnetic susceptibility of **1** arises only from the second-order Zeeman effect between the non-magnetic ground state and the higher magnetic levels, the value of the TIP being 3110 x 10^{-6} cm^3 mol^{-1}.

Experimental Section

Materials

The reagents used to the synthesis were commercially available and they were used without further purification. The [ReCl$_3$(MeCN)(PPh$_3$)$_2$] [23] and [ReOCl$_3$(PPh$_3$)$_2$] [24] complexes were prepared according to the literature method.

Instrumentation

IR spectrum was recorded on a Nicolet iS5 spectrophotometer in the spectral range 4000-400 cm^{-1} with the sample in the form of KBr pellets [Figures S1 in the Supporting Information]. X-ray powder diffraction (XRPD) measurements [Figures S2 in the Supporting Information] were performed on a PANalytical Empyrean X-ray diffractometer using Cu−Kα radiation (λ = 1.5418 Å), in which the X-ray tube was operated at 40 kV and 30 mA ranging from 5 to 50°. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 295 K on a Bruker Advance 500 NMR spectrometer with resonance frequencies of 500 MHz for ^{1}H NMR spectra and 125 MHz for ^{13}C NMR spectra by using DMSO-d$_6$ as solvent and TMS as an internal solvent[Figures S3 in the Supporting Information]. The X-ray diffraction data of **1** were collected on Oxford Diffraction four-circle diffractometer Gemini A Ultra with Atlas CCD detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented

in SCALE3 ABSPACK scaling algorithm[25] were applied. The structure was solved by the Patterson method using SHELXS97 and refined by full-matrix least-squares on F^2 using SHELXL97.[26] All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters, d(C–H) = 0.93 Å, U_{iso}(H) = 1.2 U_{eq}(C) (for aromatic); and d(C–H) = 0.96 Å, U_{iso}(H) = 1.5 U_{eq}(C) (for methyl). The methyl groups were allowed to rotate about their local threefold axis.

CCDC-1431249 (complex **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the rhenium(III) complex

Preparation of [ReCl$_3$(tppz)]·MeCN (1)

Method A: [ReCl$_3$(MeCN)(PPh$_3$)$_2$] (0.50 g, 0.60 mmol) was added to tppz (0.23 g, 0.60 mmol) in acetonitrile (100 mL) and the reaction mixture was refluxed for 4 h. The resulting solution was reduced in volume to 10 mL and allowed to cool at room temperature. A brown crystalline precipitate of **1** was filtered off and dried in the air. X-ray quality crystals of **1** as brown prisms were obtained by slow recrystallization from acetonitrile, and collected by filtration. Yield: ca. 85%.

Method B: [ReOCl$_3$(PPh$_3$)$_2$] (0.50 g, 0.60 mmol) was added to tppz (0.23 g, 0.60 mmol) in acetonitrile (100 mL) and the reaction mixture was refluxed for 4 h. The resulting solution was reduced in volume to 10 mL and allowed to cool at room temperature. A brown crystalline precipitate of **1** was filtered off and dried in the air. X-ray quality crystals of **1** were obtained by slow recrystallization from acetonitrile, and collected. Yield: ca. 70%.

Anal. calcd for C$_{21}$H$_{16}$ClN$_2$O$_6$Re (**1**): C, 41.08; H, 5.77; N, 4.56. Found: C, 40.94; H, 5.71; N 4.64%. ^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 7.69-7.56 (m, 4H), 7.52 (d, J = 19.0 Hz, 2H), 7.43 (d, J = 21.3 Hz, 2H), 7.35 (s, 4H), 7.27 (s, 4H), 2.08(s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d$_6$): δ = 133.7, 133.6, 132.9, 132.7, 132.5, 132.0, 131.9, 130.7, 129.3, 129.2, 118.6, 1.6 ppm. IR (KBr, cm^{-1}): 1598w, 1586w and 1562w [ν(C=N$_{tppz}$)] and ν(C=C$_{tppz}$)].

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

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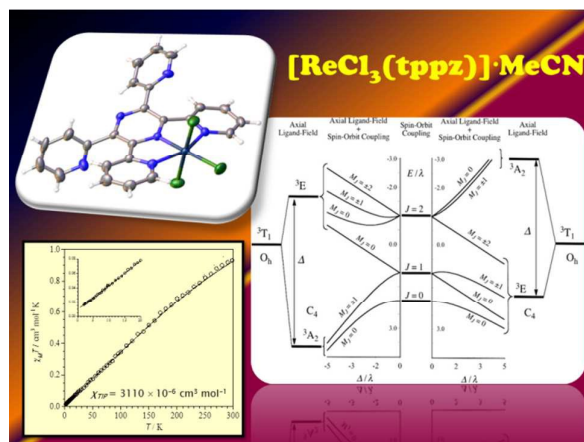
The paper reports synthesis, X-Ray structure and a deep analysis of the variable-temperature magnetic data of new complex [ReCl$_3$(tppz)]·MeCN being a very scarce example of mononuclear Re(III) complexes incorporating nitrogen donor ligands.