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Rational enhancement of the coordination capability of Ru(III)(salen)-nitronyl nitroxide building block: A step towards 2p–3d–4d magnetic edifices

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A R T I C L E I N F O

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Even if Italy won the world cup, Pr. Gatteschi's french students are glad to dedicate him this article

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A B S T R A C T

The reaction of [Ru(salen)(PPh$_3$)Cl] and the 5-imidazol-substituted nitronyl nitroxide radical (NIT-(5)ImH) yields the [Ru(salen)(PPh$_3$)(NIT-(5)ImH)](ClO$_4$) (**1**) complex which has been characterized by single crystal X-ray diffraction. This analysis reveals that the Ru(III) ion is coordinated to a tetradentate salen^{2-} ligand in equatorial positions while one PPh$_3$ ligand and one NIT-(5)ImH radical are coordinated in axial positions. This led to Ru^{III} ions in tetragonally elongated octahedral geometry. From the magnetic point of view ferromagnetic intramolecular interaction (J_1 = +2.47 cm^{-1}) have been found between the Ru(III) ion and the coordinated NIT-(5)ImH while no significant intermolecular antiferromagnetic interactions are observed at low temperature leading to a ground spin state S = 1. The absence of intermolecular magnetic interaction is explained by considering the crystal packing of (**1**) where the [Ru(salen)(PPh$_3$)(NIT-(5)ImH)]$^+$ moieties are relatively well isolated. This has to be compared with the situation observed in the previously reported [Ru(salen)(PPh$_3$)-(NIT)]$^+$ compound (**2**) where ferromagnetic Ru^{III}–NIT interaction were identified and the crystal packing generate intermolecular antiferromagnetic interactions that complicated the study. The analysis of this compound confirms the rather isotropic g values that were found of (**2**) and of [Ru(salen)(PPh$_3$)(N$_3$)], (**3**) a radical-free analogue. Moreover it is also a step towards extended structures based on Ru^{III}–NIT moieties since this compound possesses a free bischelating site likely to coordinate additional metallic ions.

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1. Introduction

Discrete or infinite polynuclear complexes with bridging ligands are widely used in the rational synthesis of molecule based magnets. Some of these polynuclear complexes can indeed present interesting physical properties as slow relaxation of the magnetization, long range magnetic ordering, conductivity, chirality, luminescence,… [1,2]. To design them different approaches have been explored during the last 20 years: one pot reactions or step by step reactions implying the use of a low-nuclearity metallic precursor. The nature of the bridging ligand is of fundamental importance in determining the obtainment of such compounds. The ligand can be a diamagnetic one, like acetato [3], cyanuro [4], oxalato [5], oxamato [6], oximato [7], and oxo [8] bridges or a paramagnetic one like TCNE (tetracyanoethenide) [9], TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) [10], nitronyl nitroxide [11], verdazyl [12] bridging radicals. This approach proved to be fruitful even when working with heavier metal ions, whose chemistry is usually rather tricky, and diamagnetic bridged complexes based on Ru(III) [13], Re(II) [14] and Re(IV) [15] have been reported. With the aim of increasing the magnetic exchange interaction in this complexes one should use ligand that possesses its own spin. Accordingly we have recently designed the first complex in which a mononuclear complex based on a heavy metal ion (Ru^{III}, (S = 1/2) was linked to a paramagnetic bridging ligand (a nitronyl nitroxide radical). More precisely the NITpPy radical (NITpPy = 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) was associated to the 4d precursor [Ru(salen)(PPh$_3$)Cl] (H$_2$salen = N,N′-ethan-1,2-diyl-bis(salicylidenamine), PPh$_3$ = triphenylphosphine) leading to the [Ru(salen)(PPh$_3$)(NITpPy)](ClO$_4$) complex [16]. Its crystallographic structure revealed a dimerization of the compound, where two [Ru(salen)(PPh$_3$)(NITpPy)]$^+$ moieties were stacked through π–π interactions between the aromatic rings of the NITpPy radical. This led to the presence of short contacts between the N–O groups of the two radicals and mediates intermolecular antiferromagnetic interaction (J = −5.0 cm^{-1}). However an intramolecular ferromagnetic interaction was found between the Ru(III) ion and the radical through the coordinated pyridine group (J = 9.0 cm^{-1}). One has to note that this compound was the first radical-based complex that

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displays 2p-Ru(III) ($S = 1/2$) ferromagnetic exchange interaction. Attempts to coordinate further this complex with 3d metal ions to built extended structures were unsuccessful given the poor reactivity of the free N–O groups.

Hence we describe in this paper the synthesis and magneto-structural characterization of a compound of formula [Ru(salen)-(PPh_3)(NIT-(5)ImH)](ClO_4) **1** (NIT-(5)ImH = 2-(5)-imidazole-4,4,5,5-tetramethylimidazoline-1-oxil-3-oxyde) where the former NitpPy radical was replaced by an imidazole substituted nitronyl nitroxide radical (noted NIT-(5)ImH). Consequently well beyond adding a new compound to the Ru^{III}-NIT family, this new compound, providing a free bischelating site is a promising building block for the synthesis of 2p–4d-based molecular magnets.

2. Experimental

[Ru(salen)(PPh_3)Cl] complex [16] and the new (2-(5)-imidazole-4,4,5,5-tetramethylimidazoline-1-oxil-3-oxyde) ligand (noted NIT-(5)ImH) are synthesized following already reported method [17]. The radical ligand was purified by chromatography on neutral alumina (Type III, ethyl acetate eluent) to give pure NIT-(5)ImH [18]. All other reagents were purchased from Aldrich and used as received.

2.1. Materials and methods

The temperature dependence of the molar magnetic susceptibility χ_M of [Ru(salen)(PPh_3)(NIT-(5)ImH)](ClO_4) **1** was investigated in the range 5–300 K in an applied magnetic field of 1 T and its magnetization at 2.7 K in the range 0–6.5 T on a Cryogenic S600 SQUID magnetometer. Data were corrected for the intrinsic diamagnetism of the sample and for a temperature independent paramagnetism (TIP) contribution of 1.0×10^{-4} $cm^3\ mol^{-1}$. X-band EPR spectra were measured on a Bruker Elexsys E500 spectrometer equipped with a continuous flow ^{4}He cryostat to work at low temperature. All measurements were performed on pellets in order to avoid in field orientation on this compound.

2.2. X-ray crystallographic analysis

X-ray data were collected at 150 K with an Oxford Diffraction Xcalibur3 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Data reduction was accomplished using CRYSALIS.RED p171.29.2 [19a]. Absorption correction was performed using both ABSGRAB and ABSPACK softwares included in the CRYSALIS package. The ABSGRAB correction allows for a determination of μ parameter ($\mu = 0.527\ mm^{-1}$). The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELXL 97 [19b]. Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms.

2.3. Preparation of [Ru(salen)(PPh_3)(NIT-(5)ImH)](ClO_4) 1

332.5 mg of Ru(salen)(PPh_3)Cl ($M = 664.5\ g\ mol^{-1}$, $n = 0.5$ mmol) are dissolved in 15 mL of CH_3OH. To this solution is added a CH_3OH solution (10 mL) containing 97.4 mg of $AgBF_4$ ($M = 194.7\ g\ mol^{-1}$, $n = 0.5$ mmol). The resulting mixture is heated under reflux during 1 h. The formed AgCl solid is removed by filtration and a CH_3OH solution (10 mL) containing 111.5 mg of NIT-(5)ImH ($M = 223\ g\ mol^{-1}$, $n = 0.5$ mmol) is added to the filtrate. The blue mixture was heated under a gently reflux for 1 h. After this delay, 306.3 mg of solid $NaClO_4$ ($M = 122.5\ g\ mol^{-1}$, $n = 2.5$ mmol) are added to the mother solution. After 5 min, a dark green crystalline powder of **1** appears. Yield: 405 mg (85%). The crystalline powder of **1** is dissolved in a minimum of CH_3OH and slow evaporation gives suitable single crystals for X-ray diffraction measurements.

Caution: Perchlorate salts are potentially explosive and should be handled with care and in small amounts [20].

3. Results and discussion

3.1. Methods and synthesis

The synthetic approach used for building [Ru(salen)(PPh_3)(NIT-(5)ImH)](ClO_4) **1** is similar to the one employed for the [Ru(salen)(PPh_3)(NITpPy)](ClO_4) complex (**2**) [16]. In fact we have previously shown that the [Ru(salen)(PPh_3)Cl] precursor is efficient to coordinate the pyridine substituted radical NITpPy [16]. As the basicity of pyridine and imidazole derivatives is very similar, we have now coordinated this same precursor to an imidazole substituted radical, hereafter NIT-(5)ImH. This change of the aromatic group is not expected to alter the nature of the magnetic interactions between the Ru(III) ion and the radical and consequently we should dispose here of a similar ferromagnetically coupled building block. Thus, **1** can be considered as a rational enhancement of the coordination capability of the previously reported [Ru(salen)(PPh_3)(NITpPy)](ClO_4) complex [16].

3.2. Description of the crystal structure

The compound **1** crystallizes in the triclinic system ($P\bar{1}$, No. 2, space group) (Table 1). An ORTEP view [21] of the corresponding asymmetric unit is shown in Fig. 1.

The Ru(III) ion is coordinated to a salen^{2-} ligand, with the two axial positions of the Ru(III) ion occupied by one PPh_3 and one NIT-(5)ImH ligands. The Ru(III) ion is localised in the plane of the salen^{2-} ligand. The electro-neutrality of the molecule is ensured by each perchlorate anion for one [Ru(salen)(PPh_3)(NIT-(5)ImH)]$^+$ mono-cationic moiety.

The four equatorial bonds Ru–X (two Ru–O_{salen} and two Ru–N_{salen}) have very similar lengths (mean lengths of 1.994 Å) while the two axial ones are longer (mean length of 2.249 Å) (see Table 2). This difference is due to the nature, the electronic density and flexibility of the donor atoms in axial and equatorial positions. The coordination polyhedron of Ru(III) ion can be thus described as an elongated octahedral geometry of tetragonal symmetry.

Table 1
Crystallographic data for [Ru(salen)(PPh_3)(NITImH)](ClO_4)

Compound	[Ru(salen)(PPh_3)(NITImH)](ClO_4)
Formula	$C_{44}H_{44}N_6O_8Cl_1P_1Ru_1$
M (g mol^{-1})	953.35
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Cell parameters	
a (Å)	10.110(5)
b (Å)	14.367(5)
c (Å)	16.696(5)
α (°)	111.799(5)
β (°)	91.875(5)
γ (°)	106.041(5)
V (Å^3)	2139.0(14)
Cell formula units, Z	2
T (K)	293(2)
Diffraction reflection	$7.72° \leqslant 2\theta \leqslant 41.62°$
ρ_{calc} (mg/m^3)	1.480
μ (mm^{-1})	0.527
Number of reflections	14547
Independent reflections	4435
$F_o > 4\sigma(F_o)$	2053
Number of variables	554
R_1, wR_2	0.0943, 0.2152

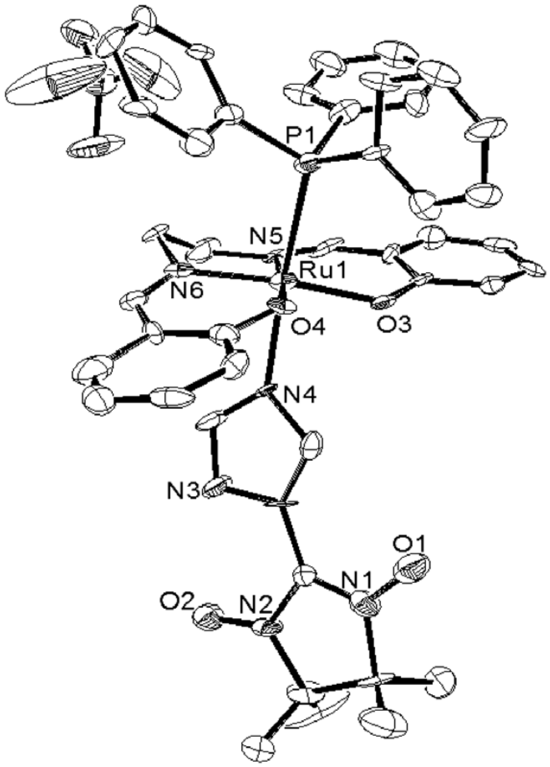

Fig. 1. ORTEP view of the asymmetric unit of [Ru(salen)(PPh_3)(NITImH)](ClO_4) with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) for [Ru(salen)(PPh_3)(NITImH)](ClO_4)

[Ru(salen)(PPh_3)(NITImH)](ClO_4)	
Ru1–$O3_{salen}$	1.977(9)
Ru1–$O4_{salen}$	1.997(10)
Ru1–$N5_{salen}$	2.004(14)
Ru1–$N6_{salen}$	1.999(13)
Ru1–$N4_{NITHIm}$	2.140(10)
Ru1–P1	2.358(4)
N1–O1	1.295(14)
N2–O2	1.278(15)
Ru1–Ru1	8.332(34)

The coordinated salen^{2-} and triphenylphosphine ligands interact together through π stacking interaction [22] between the phenyl rings of the triphenylphosphine and the salen^{2-}. The plane–plane distance is equal to 3.45 Å. The salen^{2-} ligand coordinated to the Ruthenium cation is not planar and the two aromatic rings form an angle of about 166°. This distortion is due to the proximity of a non-planar phenyl group of the triphenylphosphine (at a distance of 3.53 Å). It also permits to increase the distance between the aromatic system of the tetradentate ligand and the phenyl group and so to decrease the repulsion/steric hindrance between these two groups. The coordinated NIT-(5)ImH ligand is quasi planar with a torsion angle close to 0° (4.5°) between both imidazole and the imidazoline cycles. Hydrogen bonds are found between the hydrogen atom localised on the N3 nitrogen atom and the O2 oxygen (2.149 Å). A second one involves the same hydrogen atom but with the O6 oxygen of the perchlorate anion (2.097 Å). An analysis of the crystal packing (Fig. 2) shows that the interactions between the radical ligands NIT-(5)ImH are very small and the shortest N–N and N–O distances are of 4.715 and 4.824 Å, respectively.

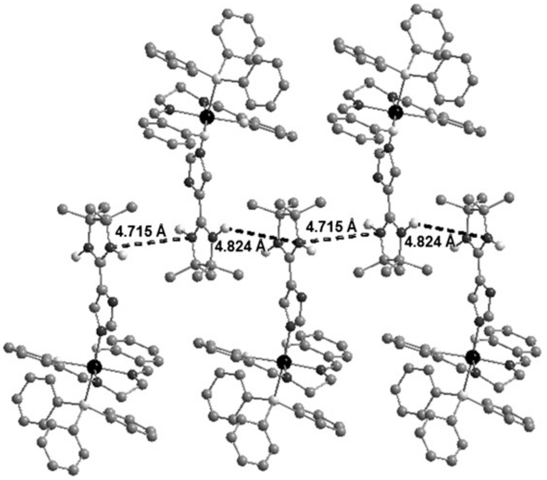

Fig. 2. Packing view of [Ru(salen)(PPh_3)(NITImH)](ClO_4) showing the shortest intermolecular distances between the nitronyl nitroxide radicals.

In summary, the crystallographic structure of **1** is very similar to the one of the already reported [Ru(salen)(PPh_3)(NITpPy)](ClO_4) complex. The Ru–X distances, the conformation of the salen^{2-} and the interactions between the salen^{2-} and PPh_3 ligands are very close in both structures. The fundamental difference between the two structures is the packing of the molecules in the crystal. Indeed, the substitution of the pyridine group by an imidazole group leads to a drastic change of interactions between the radical ligands. In the packing of **1**, no significant interactions between the nitronyl nitroxide are found while for [Ru(salen)(PPh_3)(NITpPy)](ClO_4) a dimerization of the molecules has been reported. This dimeric structure led to short contacts between the nitronyl nitroxide ligands that considerably affect the magnetic properties of the complex.

3.3. *EPR study*

The X-band EPR spectrum of **1** at 5 K is reported in Fig. 3. It consists of an intense and partially asymmetric band (ΔH_{pp} = 120 Oe) centered around g = 2.01. The observed g value is compatible with that observed in [Ru(salen)(PPh_3)(NITpPy)] derivative (**2**), whereas the linewidth is much smaller. The first feature is a consequence of both the quasi-isotropic ligand field around Ru(III), as suggested by the EPR spectrum of the related Ru(salen)(PPh_3)(N_3)] [16] complex (**3**), and of the contribution of the radical spin to the active EPR state. On the other hand, the increased sharpness of the band should be attributed to the absence of the strong intramolecular interaction between two Ru–NIT moieties with mutually

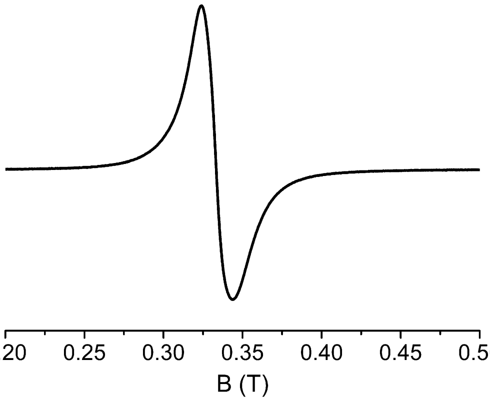

Fig. 3. X-band (9.364 GHz) EPR spectrum of a powder sample of [Ru(salen)(PPh_3)(NITImH)](ClO_4) measured at 5 K.

perpendicular elongation axis observed in [Ru(salen)(PPh_3)(NIT-pPy)](ClO_4). Finally, it is interesting to note that the spectrum does not show evidence for a fine structure. This suggests that, if present, any zero field splitting of the resulting triplet state should be small.

3.4. Magnetic properties

The thermal variations of the molar magnetic susceptibility χ_M and the $\chi_M T$ product of **1** are shown in the Fig. 4. χ_M versus T curve shows a continuous increase from 300 to 5 K while the $\chi_M T$ product takes a constant value of 0.79 cm^3 K mol^{-1} from 300 to about 75 K. Below 75 K, this latter increases to take the value of 0.89 cm^3 K mol^{-1} at 5 K (inset of Fig. 4). The observed value at room temperature is in agreement with what expected for one NIT-(5)ImH radical ($S = 1/2$, $g = 2.00$) and one Ru(III) ion with g slightly larger than 2.00, as observed in other compounds containing low spin state Ru(III) ions [16,23]. The shape of the $\chi_M T$ versus T curve is characteristic of a dominant ferromagnetic interaction below 75 K.

Fig. 5 shows the experimental magnetization of **1** and the calculated Brillouin function [1] at 2.7 K assuming one uncorrelated $S = 1/2$ with $g = 2.00$ (nitronyl nitroxide radical) and one uncorrelated $S = 1/2$ with $g = 2.05$ (Ru(III) ion). For any field, the experimental magnetization of **1** is higher than that of the uncorrelated system. This comparison confirms the presence of a ferromagnetic exchange interaction that can be assigned to the intramolecular Ru(III)-NIT-(5)ImH exchange pathways has for the previously reported compound. This statement can be rationalized considering that the ground state of Ru(III), as evidenced by the EPR spectrum of [Ru(salen)(PPh_3)(N_3)] (**3**) [16], is characterised by a relevant contribution of the $4d_{xy}$ magnetic orbital of Ru(III) ion. Consequently the Ru(III)-radical ferromagnetic interaction can be attributed to the orthogonality of this orbitals with the $2p_z$ magnetic orbitals of the NIT-(5)ImH radical.

A quantitative determination of the molar magnetic susceptibility is performed by fitting the data through a Bleaney–Bowers expression [1], the interaction of NIT-(5)ImH and Ru(III) with the magnetic field being considered to be isotropic (cf. EPR measurements). The experimental χ_M curve has been fitted in the 5–300 K range with a mean value of g for the complex **1**. We note here that, while in principle the use of isotropic exchange hamiltonian is not perfectly justified for systems containing orbitally degenerate centres, the largely isotropic nature of Ru(III) centers evidenced by the EPR spectrum of [Ru(salen)(PPh_3)(N_3)] (**3**) [16] justifies this approach [24]. The best fit ($R = 0.999$, Fig. 4) highlights a ferromagnetic interaction between the Ru(III) ion and the coordinated NIT-(5)ImH ligand ($J = +2.47 \pm 0.07$ cm^{-1}, $H = -JS_{Ru}S_{NIT-(5)ImH}$) considering the mean g value $g = 2.05$. The difference with the g value obtained by EPR, of 2%, probably reflects a sample weighing error, and is then physically unrelevant.

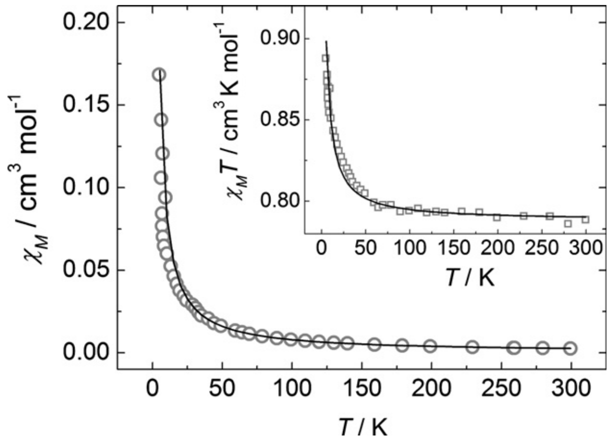

Fig. 4. Plot of χ_M vs T for [Ru(salen)(PPh_3)(NITImH)](ClO_4) (grey circles) measured at 1 T and its best fit in full black line. In the inset is shown the experimental product $\chi_M T$ vs T (grey squares) and its best fit in full black line for [Ru(salen)(PPh_3)(NITImH)](ClO_4) measured at 1 T.

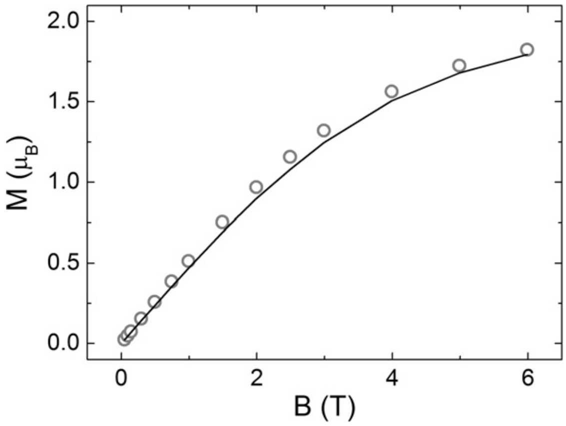

Fig. 5. The experimental (grey circles) and calculated magnetization (full black line) for [Ru(salen)(PPh_3)(NITImH)](ClO_4) at 2.7 K in field range 0–6 T.

The ferromagnetic interaction found in **1** is smaller than that in [Ru(salen)(PPh_3)(NITpPy)](ClO_4) ($J = +\ 9.00$ cm^{-1}) probably due to an electronic delocalisation on the coordinated nitrogen atom of the imidazole ring that is weaker than the one of the pyridine derivative. However in **1** no antiferromagnetic interaction is observed at low temperature contrary to what seen on [Ru(salen)(PPh_3)(NITpPy)](ClO_4) [16]. As already suggested this is due to the crystal packing of **1**, where the insulation of the molecule is drastically enhanced since no N–O···O–N contacts are present here. Consequently the spin state at low temperature of **1** is $S = 1$ when it was $S = 0$ for [[Ru(salen)(PPh_3)(NITpPy)](ClO_4)]$_2$.

4. Conclusion

In summary, we have synthesized and characterized by X-ray diffraction a new Ru(III)–Nitroxide complex where ferromagnetic exchange interactions have been found between the Ru(III) ion and the radical ligand. The appropriate choice of a new nitronyl nitroxide radical coordinated on the Ru(III) ion has permitted to suppress the intermolecular antiferromagnetic interaction observed in our previously reported complex [Ru(salen)(PPh_3)(NIT-pPy)](ClO_4) (**2**). Compound **1** is thus a $S = 1$, 2p–4d, building block, where the free bis-chelating coordination site is likely to coordinate additional metallic ions to form extended structures. Synthesis of heterometallic 2p–3d–4d complexes based on the precursor **1** are in progress.

Acknowledgments

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Appendix A. Supplementary material

CCDC 674627 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.02.047.

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