Synthesis, X-ray crystal structures and magnetic properties of Cu^{II} and Mn^{II} complexes containing imino nitroxide radicals and a dicyanamide anion

Iwayan Dasna,†[a] Stéphane Golhen,[a] Lahcène Ouahab,*[a] Nathalie Daro[b] and Jean-Pascal Sutter[b]

[a] *Laboratoire de Chimie du Solide et Inorganique Moléculaire (CNRS UMR 6511), Institut de Chimie de Rennes, Université de Rennes 1, Campus Beaulieu 35042, Rennes cedex, France. E-mail: ouahab@univ-rennes1.fr*

[b] *Laboratoire des Sciences Moléculaires (CNRS UPR 9048), ICMCB, 33608 Pessac, France*

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Two new complexes having the formula *cis*-Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$ (**1**) and Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$ (**2**), where imi-pPy stands for 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, were synthesized and structurally and magnetically characterized. The two compounds **1** and **2** crystallize in the space groups $C2/c$ (no. 15) and $P\bar{1}$ (no. 2), respectively. The metal atoms are in a distorted octahedral geometry. **1** presents a 1D infinite chain structure and **2** has a finite structure. Antiferromagnetic interactions are observed in the Cu containing salt while ferromagnetic interactions are observed in the Mn compound but antiferromagnetic interactions dominate at very low temperature.

Polymeric coordination compounds based on polycyanide ligands are the subject of numerous investigations because of the strong ability of these ligands to act as a magnetic coupler between paramagnetic transition metals.[1–8] The best known examples are the ferromagnets of general formula $\{M[N(CN)_2]_2\}$ with a 3D rutile-type structure containing the dicyanamide anion $N(CN)_2^-$ [1,2] and the Prussina blue derivatives with a 3D face-centered cubic structure involving CN^- groups.[3] These compounds consist of paramagnetic metal ions covalently linked by μ_1, μ_2, μ_3 or μ_4 bridging ligands. The bridging ligands may be diamagnetic such as the linear silver cyanide anion $[Ag(CN)_2]^-$,[1c] bent dicyanamide anion $[N(CN)_2]^-$,[1,2] trigonal tricyanomethide anion $[C(CN)_3]^-$,[4] tetracyanometallate dianions $[M(CN)_4]^{2-}$,[5] paramagnetic heptacyanometallate anions $[Mo(CN)_7]^{4-}$,[6] hexacyanometallate anions $[M(CN)_6]^{3-}$ where $M = Fe^{III}$, Cr^{III},[3] or an organic radical anion such as TCNE or TCNQ.[7] We are investigating such kinds of materials by including paramagnetic nitroxide radicals in the coordination sphere of the metal with the aim of increasing the magnetic moments of the starting complexes. Some paramagnetic nitroxide radicals are known as all-organic ferromagnets at very low temperature.[9] They are also used as bridging ligands between metal ions in magnetic materials.[10] We reported recently some compounds of this type. Mn(NITpPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$, where NITpPy stands for 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, shows a 0D structure, *i.e.* is isolated/discrete molecules; Mn^{II}(NITpPy)$_4$[N(CN)$_2$]$_2$[2a] and Mn^{II}(NITpPy)$_2$[Ag(CN)$_2$]$_2$[11] have 1D structures while Mn(NITpPy)$_2$[N(CN)$_2$]$_2\cdot$2CH$_3$CN presents a 2D layered structure associated with ferromagnetic interactions.[12] In order to appreciate the inflence of the nature of the organic radical on the structural and magnetic properties of the target complexes, we investigated compounds containing the imino nitroxide radical instead of the nitronyl nitroxide radical and we report here the synthesis, X-ray crystal structures and magnetic properties of two new complexes of formula *cis*-Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$ (**1**) and Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$ (**2**). Compound **1** presents an infinite 1D chain structure but compound **2** has a 0D structure and ferromagnetic interactions are observed in the Mn complex while antiferromagnetic interactions are observed in the Cu complex.

Experimental

Synthesis

NaN(CN)$_2$, Cu(NO$_3$)$_2\cdot$2.5H$_2$O, Mn(NO$_3$)$_2\cdot$6H$_2$O (Aldrich) were used as purchased. imi-pPy was prepared as previously described.[13] All experiments were conducted under argon using freshly distilled solvents. Stoichiometries were fixed by X-ray crystal structure analysis.

***cis*-Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$ (1).** Cu(NO$_3$)$_2\cdot$2.5H$_2$O (0.2326 g, 1 mmol) was dissolved in 5 ml methanol and added to a 5 ml methanol solution of 0.4378 g (2 mmol) of imi-pPy with stirring at 50 °C for 2 h NaN(CN)$_2$ (0.1785 g, 2 mmol) was dissolved in a mixture of 4 ml methanol and 1 ml H$_2$O. The mixture of the two solutions was stirred for 6 h at 50 °C. The solution was then filtered and the orange precipitate was washed with methanol and recrystallized in acetonitrile by slow evaporation in air. Yield 57% IR (KBr): $\nu_{C\equiv N}$ 2294(m), 2239(m), 2182(s); $\nu_{N\text{–}O}$ 1362(w); ν_{py} 1619(m), 1545(w), 1451(m), 1419(w) cm^{-1}.

Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$ (2). Mn(NO$_3$)$_2\cdot$6H$_2$O (0.2870 g, 1 mmol) was dissolved in 5 ml of water and added to a 10 ml water solution of imi-pPy (0.4378 g, 2 mmol) with stirring at room temperature for 2 h. NaN(CN)$_2$ (0.1785 g, 2 mmol) was dissolved in 5 ml H$_2$O. The mixture of the two

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† Permanent address: Jurusan Kimia, FMIPA, Universitas Negeri Malang, Jl. Surabaya 6, Malang 65145, Indonesia.

solutions was stirred overnight, giving a yellow–orange precipitate and an orange solution. The precipitate was collected by fitration, washed with water and recrystallized twice in hot methanol yielding (73%) parallelepipedic orange crystals. Additional crystals were obtained from the filtrate by slow evaporation over the course of a week. IR (KBr): ν_{N-O} 1142(w), 1373(m); $\nu_{C\equiv N}$ 2284(s), 2234(m), 2160(vs); ν_{py} 1616(m), 1542(w), 1451(m) cm^{-1}.

Crystallographic data collection and structure determination

Single crystals of the title compounds (**1**,**2**) were mounted on an Enraf–Nonius four-circle diffractometer equipped with a CCD camera and a graphite monochromated Mo-Kα radiation source ($\lambda = 0.71073$ Å). Data collection was performed at room temperature. No absorption corrections were performed and structures were solved with SHELXS-97 and refined with the SHELXL-97 program[14] by full-matrix least-squares methods on F^2. Crystallographic data are summarized in Table 1, selected bond distances and bond angles are given in Table 2.

CCDC references numbers 164372 and 164373. See http://www.rsc.org/suppdata/nj/bl/b104773f/ for crystallographic data in CIF or other electronic format.

Magnetic and spectroscopic measurements

Magnetic studies were carried out on powdered microcrystalline samples enclosed in a medical cap. Magnetic susceptibility measurements were performed with a MPMS-5 SQUID magnetometer from Quantum Design Corporation. The temperature dependence of the magnetic susceptibility for the title compounds was measured in the temperature range 2–300 K, with an applied field of 1000 Oe.

IR characterizations were performed on KBr pellet samples with a Brucker Equinox 55 spectrometer.

Results and discussion

Crystal structures

***cis*-Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$ (1).** The Cu atom is located on a mirror plane and adopts a distorted octahedral coordination [Fig. 1(a)]. It is bonded in the equatorial square plane to two radicals and two N(CN)$_2$$^-$ anions, both in *cis* positions; the apical positions are occupied by N(CN)$_2$$^-$ ligands belonging to two adjacent molecules, giving rise to a 1D infinite chain along the *c* axis [Fig. 1(b)]. The Cu atom is bonded to the imi-pPy radicals through the N atom of the pyridyl rings with Cu–N1 bond lengths of 2.027(3) Å and a N1–Cu–N1 bond angle of 89.46(15)°. The angle between the pyridyl ring and the nitroxide group is 26.8(2)°. The oxygen atom O1 is distributed on the two sides of the nitroxide group (N2 and N3) with occupancy factors equal to 0.81 and 0.19, respectively. The [N(CN)$_2$]$^-$ anions act as μ_2 bridging ligands. The intramolecular Cu···N4 [N(CN)$_2$] bond length and Cu–N4–C13 angle are equal to 1.984(3) Å and 159.3(3)°, while the intermolecular Cu···N6 [N(CN)$_2$] bond length and Cu–N6–C14 angle are equal to 2.546(3) Å and 108.9(2)°, respectively. The N4–Cu–N4 and N1–Cu–N4 angles are equal to 89.77(18) and 90.40(12)°, respectively. The intra- and interchain Cu–Cu distances are 7.158(2) and 6.709(1) Å.

Table 1 Crystal data and structure refinement for **1** and **2**

	1	2
Formula	$C_{56}H_{64}Cu_2N_{24}O_4$	$C_{28}H_{36}MnN_{12}O_4$
Formula weight	1264.39	659.63
T/K	293(2)	293(2)
Crystal system	Monoclinc	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	22.2730(11)	7.1089(2)
b/Å	23.3463(12)	9.9495(3)
c/Å	7.1583(2)	13.2518(6)
α/°	90.0	69.396(1)
β/°	93.960(3)	88.999(1)
γ/°	90.0	71.461(2)
U/Å^3	3713.4(3)	827.09(5)
Z	2	1
μ/mm^{-1}	0.627	0.451
Total reflect.	7350	6724
Unique reflect.	4096	3787
R(int)	0.0278	0.0289
R_1	0.0594	0.0462
wR_2 [$I > 2\sigma(I)$]	0.1931	0.1201
R_1	0.0805	0.0672
wR_2 (all data)	0.2081	0.1378

Table 2 Selected bond lengths (Å) and angles (°) for **1** and **2**

	Compound 1		
Cu(1)–N(4)	1.984(3)	N(4)–C(13)	1.146(4)
Cu(1)–N(1)	2.027(3)	C(13)–N(5)	1.295(5)
N(1)–C(1)	1.332(4)	C(14)–N(5)	1.301(5)
N(1)–C(5)	1.344(4)	C(14)–N(6)	1.155(4)
N(2)–O(1A)	1.234(5)	N(2)–C(6)	1.357(5)
N(3)–C(6)	1.302(5)	N(2)–C(8)	1.498(5)
N(3)–O(1B)	1.34(2)	N(3)–C(7)	1.485(5)
C(3)–C(6)	1.480(5)	C(7)–C(8)	1.525(7)
N(4)–Cu(1)–N(1)	90.40(12)	C(2)–C(3)–C(6)	123.4(3)
C(1)–N(1)–C(5)	117.6(3)	C(6)–N(3)–O(1B)	127.1(11)
C(1)–N(1)–Cu(1)	120.6(2)	C(6)–N(3)–C(7)	108.5(3)
C(5)–N(1)–Cu(1)	121.8(2)	O(1B)–N(3)–C(7)	113.8(9)
N(1)–C(5)–C(4)	122.6(3)	N(3)–C(6)–N(2)	113.6(3)
C(5)–C(4)–C(3)	119.7(3)	N(3)–C(6)–C(3)	122.7(3)
O(1A)–N(2)–C(6)	128.4(3)	N(2)–C(6)–C(3)	123.8(3)
O(1A)–N(2)–C(8)	122.3(3)	C(13)–N(4)–Cu(1)	159.3(3)
C(6)–N(2)–C(8)	109.1(3)	N(4)–C(13)–N(5)	173.8(4)
C(4)–C(3)–C(2)	117.5(3)	N(6)–C(14)–N(5)	174.4(4)
C(4)–C(3)–C(6)	119.1(3)	C(13)–N(5)–C(14)	120.3(3)
	Compound 2		
Mn–O(1W)	2.1722(15)	N(3)–C(6)	1.313(3)
Mn–N(4)	2.2012(18)	C(6)–N(2)	1.355(3)
Mn–N(1)	2.285(2)	N(1)–C(5)	1.338(3)
N(1)–C(1)	1.337(3)	C(13)–N(5)	1.284(3)
O(1A)–N(2)	1.211(4)	N(5)–C(14)	1.307(3)
O(1B)–N(3)	1.191(7)	N(4)–C(13)	1.151(3)
C(14)–N(6)	1.140(3)		
O(1W)–Mn–N(4)	90.54(7)	C(6)–N(3)–C(8)	108.7(2)
O(1W)–Mn–N(1)	92.96(7)	N(3)–C(6)–C(3)	123.3(2)
N(4)–Mn–N(1)	88.51(7)	C(13)–N(4)–Mn	150.6(2)
O(1B)–N(3)–C(6)	128.2(5)	C(5)–N(1)–C(1)	116.8(2)
N(3)–C(6)–N(2)	113.6(2)	C(5)–N(1)–Mn	121.70(15)
C(6)–N(2)–O(1A)	128.4(3)	C(1)–N(1)–Mn	121.44(15)
O(1A)–N(2)–C(7)	122.3(3)	N(4)–C(13)–N(5)	171.4(2)
C(6)–N(2)–C(7)	109.2(2)	N(6)–C(14)–N(5)	173.0(3)
N(2)–C(6)–C(3)	123.1(2)	C(13)–N(5)–C(14)	123.8(2)
O(1B)–N(3)–C(8)	118.7(4)		

Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$ (2). The structure of this compound is similar to its analogue containing nitronyl nitroxide radicals instead of imino radicals.[12] The Mn atom is located on an inversion centre and adopts a distorted octadhedral coordination [Fig. 2(a)]. Due to centring both radicals, anions and water molecules are in *trans* positions. The Mn atom is bonded to the imi-pPy radicals through the N atom of the pyridyl rings with Mn–N1 bond lengths of 2.285(2) Å. The angle between the pyridyl ring and the nitroxide group is 27.9(2)°. In this compound the [N(CN)$_2$]$^-$ anions act as terminal ligands. The Mn–N4 [N(CN)$_2$] and Mn–O1W (H$_2$O) bond lengths are equal to 2.201(2) and 2.172(2) Å, respectively. The values of Mn–N4≡C13 and N5–C13≡N4 angles are equal to 150.6(2) and 171.4(2)°, respectively, and deviate from linearity

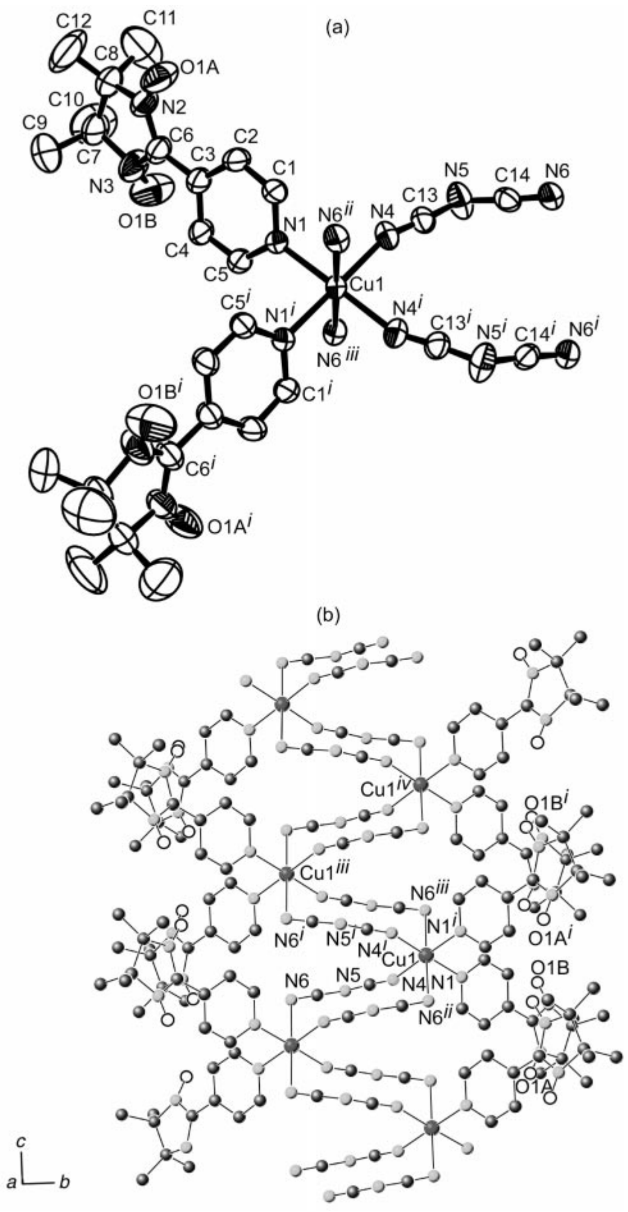

Fig. 1 Compound **1**: (a) molecular structure with 50% probability ellipsoids; (b) crystal structure with shortest contacts. Symmetry transformations used to generate equivalent atoms: *i*: $1-x$, y, $0.5-z$; *ii*: $1-x$, $-y$, $-z$; *iii*: x, $-y$, $0.5+z$; *iv*: x, y, $1+z$.

but are in the range of what was found in similar compounds.[12] The oxygen atom O1 is distributed over the two positions of the nitroxide group with occupancy factors equal to 0.70 and 0.30. The shortest contacts between nitroxide groups are $\mathrm{O1B}^{vi}$–$\mathrm{O1B}^{iv} = 3.72(2)$ Å, with $\mathrm{N3}^{vi}$–$\mathrm{N3}^{iv}$ and $\mathrm{O1B}^{vi}$–$\mathrm{O1A}^{vii}$ being respectively equal to 4.578(6) and 3.872(2) Å [Fig. 2(b)]. Intermolecular short contacts are observed between the co-ordinated water molecule O1w and the non-co-ordinated N atoms of the $\mathrm{N(CN)_2}^-$ ligand [O1W–N5 = 2.865(2); O1W–N6 = 2.767(2) Å], indicating the existence of hydrogen bonding.

Magnetic properties

The plots of $\chi_M T$ *versus T*, where χ_M is the molar magnetic susceptibility corrected for the core diamagnetism[15] and T the temperature, are shown in Fig. 3 and 4 for Cu(imi-pPy)$_2$-[N(CN)$_2$]$_2$, **1**, and Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$, **2**, respectively.

At 300 K for compound **1** the value of $\chi_M T$ is equal to 1.12 cm^3 K mol^{-1}, a value consistent with three uncorrelated $S = 1/2$ spins. When the temperature is lowered this value

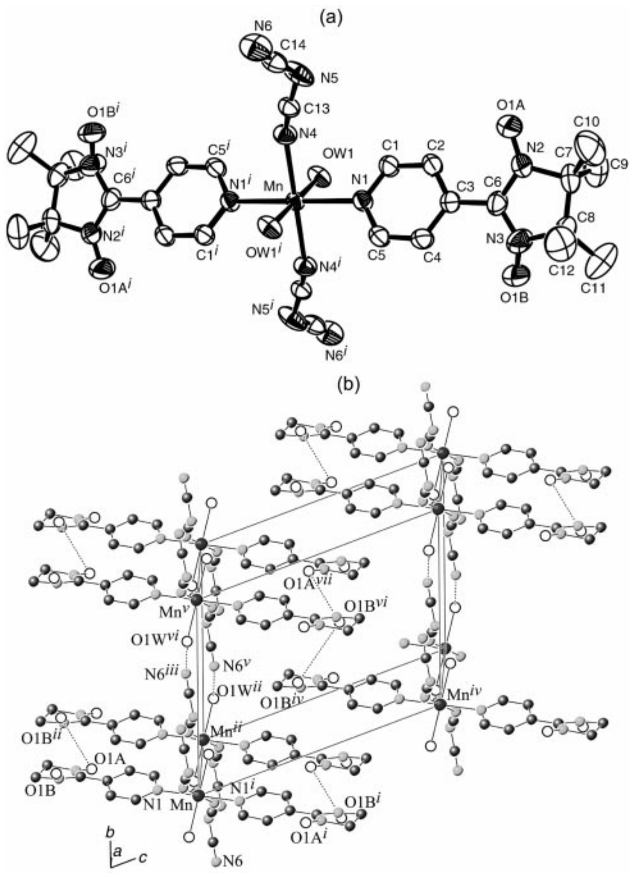

Fig. 2 Compound **2**: (a) molecular structure with 50% probability ellipsoids; (b) crystal structure with shortest contacts. Symmetry transformations used to generate equivalent atoms: *i*: $-x$, $-y$, $-z$; *ii*: $1+x$, y, z; *iii*: $1-x$, $-y$, $-z$; *iv*: x, y, $1+z$; *v*: x, $y+1$, z; *vi*: $-x$, $1-y$, $-z$; *vii*: $1-x$, $1-y$, $-z$.

decreases more and more rapidly, a feature indicative of antiferromagnetic interactions attributed to the intramolecular Cu–radical interaction, as observed in related compounds.[10c,16] Indeed, the profile of the $\chi_M T$ *versus T* curve could be well reproduced by a model derived from the spin Hamiltonian $H = -J(\boldsymbol{S}_{\mathrm{Cu}} \cdot \boldsymbol{S}_{\mathrm{rad1}} + \boldsymbol{S}_{\mathrm{Cu}} \cdot \boldsymbol{S}_{\mathrm{rad2}})$. The continuous decrease of $\chi_M T$, even for low temperatures, is attributed to weak exchange interactions taking place between the Cu-(Imino)$_2$ units. Therefore, a weak interaction based on the mean-field approximation, zJ', was introduced. The best fit to the experimental data (Fig. 3) yielded $J = -9.0 \pm 0.3$ cm^{-1}

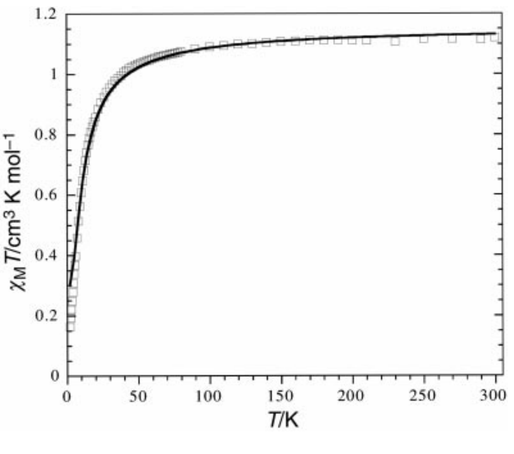

Fig. 3 Experimental (□) and calculated (—) $\chi_M T$ *versus T* behaviour for {Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$}, **1**.

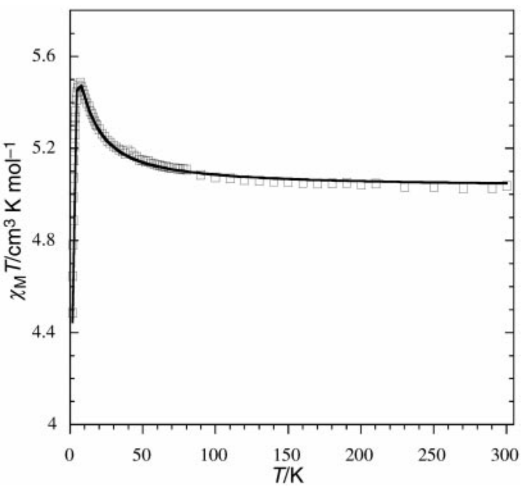

Fig. 4 Experimental (□) and calculated (—) $\chi_M T$ *versus* T behaviour for {Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$ · 2H$_2$O}, **2**.

for the Cu(II)–imino radical interaction parameter, $zJ' = -1.5$ cm^{-1} (fixed) and $g = 2.025 \pm 0.006$.

For Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$, **2**, $\chi_M T$ is equal to 5.12 cm^3 K mol^{-1}, the expected value for isolated $S_{Mn} = 5/2$ and two $S_{rad} = 1/2$ spins. As the temperature is lowered, $\chi_M T$ increases to reach a maximum of 5.48 cm^3 K mol^{-1} at 7 K, and then decreases rapidly to about 4.64 cm^3 K mol^{-1} at 2 K (Fig. 4). The profile of the curve is consistent with ferromagnetic interactions attributed to the intramolecular Mn–radical interaction, as observed in related compounds.[8b,10f,g,12] The decrease of $\chi_M T$ below 7 K indicates that weak antiferromagnetic interactions take place between the Mn(Imino)$_2$ units. It is likely that these interactions result from the proximity of the radical units of neighbouring molecules as revealed by the X-ray analysis; however, based on the structural features they are expected to be weak.[17] Therefore, the temperature dependence of the magnetic susceptibility was reproduced with an expression of χ_M taking into account the interaction between the Mn(II) ion and the two paramagnetic ligands, a theoretical expression deduced from the spin Hamiltonian $H = -J(\boldsymbol{S}_{Mn} \cdot \boldsymbol{S}_{rad1} + \boldsymbol{S}_{Mn} \cdot \boldsymbol{S}_{rad2})$. The intermolecular exchange interaction was considered in the mean-field approximation as zJ'. Least-squares fitting of the experimental data led to $J = 1.64 \pm 0.01$ cm^{-1} and $zJ' = -0.17$ cm^{-1} (g_{Mn} and g_{rad} were taken an equal to 2.00).

The magnetic behaviours of Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$, **1**, and Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$, **2**, are in agreement with the behaviours previously observed for related nitronyl nitroxide derivatives.[8b,11,16] However, it should be noted that the M–imino radical interaction parameters found for compound **1**, $J = -9.0$ cm^{-1}, and compound **2**, $J = 1.64$ cm^{-1}, are somewhat smaller than those obtained for their nitronyl nitroxide counterparts. In compound **1**, each N(CN)$_2$ ligand bridges two [Cu(imino-pPy)$_2$] magnetic clusters through an axial co-ordination to one Cu(II) whereas its link to the second is equatorial to that ion. Such a co-ordination scheme should lead to antiferromagnetic interactions between the Cu(II) centres. The exchange parameter (-1.5 cm^{-1}) found for **1** is in line with the anticipated behaviour.

Conclusions

Two new complexes, formulated as *cis*-Cu(imi-pPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$ (**1**) and Mn(imi-pPy)$_2$[N(CN)$_2$]$_2$(H$_2$O)$_2$ (**2**), were obtained and structurally and magnetically characterized. For both compounds Cu and Mn atoms present a distorted octahedral geometry. One of the objectives of this work was to investigate the influence of the modification of the organic radical on the structural and magnetic properties of the target complexes. Comparison of the results found here with those previously reported for the nitronyl nitroxide (NITpPy) containing complexes shows that the structures and magnetic properties are only slightly altered when the organic radical is changed from nitronyl nitroxide to its imino nitroxide analogue. Compound **1** displays infinite 1D structures but compound **2** has a discrete structure. The magnetic characteristics of both compounds are mainly governed by the behaviour of the M(radical)$_2$ units. For the Cu derivative **1** an overall antiferromagnetic behaviour has been found whereas for Mn derivative **2** the magnetic properties revealed intramolecular ferromagnetic interactions between the Mn(II) and the paramagnetic ligand, although with the overall magnetic behavior being governed by intermolecular interactions at low temperature with dominant antiferromagnetic interactions. As for other related compounds reported previously,[11,12] these results indicate that the [N(CN)$_2$]$^-$ ligand does not (or does only very weekly) mediate the magnetic communication between the M(imi-pPy)$_2$ units. This is rather unexpected and contrasts with the rutile-type compounds based on the [N(CN)$_2$]$^-$ ligand, which show magnetic interactions.[1] It will be noticed that the N atom bridging the two (CN)$^-$ groups of the [N(CN)$_2$]$^-$ ligand is not involved in any co-ordination to a paramagnetic unit; this could account for the poor exchange interactions within the network.

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