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FULL PAPER

1-D mixed stack of coordinated and uncoordinated radicals in $Mn^{II}(NITpPy)_4[N(CN)_2]_2$ (NITpPy = nitronyl nitroxide radical)

Iwayan Dasna,[a] Stéphane Golhen,[a] Lahcène Ouahab,*[a] Octavio Peña,[a] Joseph Guillevic[a] and Mohammed Fettouhi[b]

[a] *Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511, Université de Rennes 1, Campus Beaulieu 35042, Rennes cedex, France*
[b] *Chemistry Department, King Fahd University of Petroleum and Minerals, P.O. Box 5048, Dahran 31261, Saudi Arabia*

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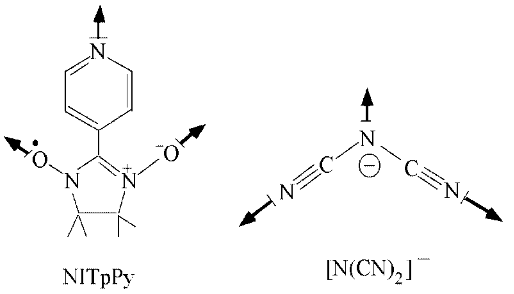
The synthesis, X-ray crystal structures and magnetic properties of the 1-D polymeric coordination compound $Mn^{II}(NITpPy)_4[N(CN)_2]_2$ (NITpPy = 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide) are reported. In the crystal structure the $[Mn^{II}(NITpPy)_2]^{2+}$ units are linked by $N(CN)_2^-$ μ-bridging ligands to form one dimensional polymeric columns. In the columns, the coordinated radicals alternate with uncoordinated ones. The magnetic properties obey a Curie–Weiss law with weak antiferromagnetic interactions.

Introduction

Richness topology and related physical properties of polymeric coordination compounds constitute a hot subject of research.[1] Thanks to the ability of linker ligands, it is possible to build by self-assembly compounds with increased dimensionality like nanoporous materials[2,3] or hard molecular magnets.[4,5] The diamagnetic cyanide anions $(CN)^-$, $[C(CN)_3]^-$, $[N(CN)_2]^-$ and other pseudohalide anions $(N_3)^-$, $(NCS)^-$, $(NCO)^-$ are successfully used in the design of materials with dimensionality ranging from 0 to 3-D associated with particular physical properties.[4–16] On the other hand, the paramagnetic NITpPy [2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide] (Scheme 1) was used as a bridging ligand between metals in many magnetic materials containing a spin residing on the d orbitals of the metals and π-orbitals of the radicals, such as $Mn(hfac)_2(NITpPy)$[17] (hfac = hexafluoroacetylacetonato) or in $[Cu(hfac)_2]_3(NITpPy)_2$.[18] In the former compound, the metal sites are μ-bridged *via* the oxygen atoms of the nitroxide groups, while they are linked in the second one *via* both the nitrogen atom of the *p*-pyridyl ring and the oxygen atoms of the NO groups.



Scheme 1 Arrows indicate possible coordination sites.

Taking advantage of the abilities of both nitroxide radicals and the above mentioned kind of anions to coordinate transition metals, we are currently investigating the synthesis of materials containing metal radical complexes linked by polycyanide anions. We are dealing with the use of the dicyanamide anions $[N(CN)_2]^-$ (Scheme 1) as bridging ligands between paramagnetic complexes $M^{II}(NITpPy)_n^{2+}$ ($M = Cu^{II}, Mn^{II}, Co^{II}$; $n = 2$–4) focusing in this work on $M = Mn^{II}$. Dicyanamide anion $[N(CN)_2]^-$ can act as a terminal ligand, it can act also as a μ, μ_3 and μ_4 bridging ligand.[4–16] We report here the synthesis, X-ray crystal structure and magnetic properties of the one dimensional polymeric compound $Mn^{II}(NITpPy)_4[N(CN)_2]_2$.

Experimental

Synthesis

$NaN(CN)_2$ (Fluka), $Mn(NO_3)_2·6H_2O$ (Aldrich) were used as purchased. NITpPy was prepared as previously described.[19] All experiments were performed under argon using freshly distilled solvents.

$Mn^{II}(NITpPy)_4[N(CN)_2]_2$. $Mn(NO_3)_2·6H_2O$ (0.287 g, 1 mmol) was dissolved in 5 ml of hot methanol (50 °C) and added to a 5 ml methanol solution of NITpPy (0.980 g, 4 mmol) leading to a blue solution. The mixture was stirred for 1 hour. To this solution was added a methanol solution of $Na[N(CN)_2]$ (0.202 g, 2 mmol) with stirring at 50 °C over 1 hour. The blue solution was kept overnight at 30 °C and blue needle crystals were isolated from the solution. Yield: 65%. Anal. obs. (calc.): C 55.06 (55.59), H 5.67 (5.70), N 22.39 (22.43), Mn 4.44 (4.89)%. Infrared spectra (KBr): $\nu_{C\equiv N}$ 2174vs, 2242m, 2298m cm^{-1}; ν_{N-O} 1371s, 1138m cm^{-1}; ν_{py} 1610m, 1547m, 1448m, 1404m cm^{-1}.

Crystallographic data collection and structure determination

A single crystal was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromated MoKα radiation source ($\lambda = 0.71073$ Å). The air-unstable crystal was protected with glue. Cell dimensions and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 centered reflections. The crystal data are summarized in Table 1. Intensities were collected by θ–2θ scans, no significant decay was revealed on the three standard reflections measured every hour during data collection. Data reductions and corrections were performed with MolEN.[20] Lorentz polarization and semi-empirical absorption corrections (ψ-scan method)[21] were applied to intensities for all data. Scattering factors and corrections for anomalous dispersion were taken from ref. 22. Structure was solved with

Table 1 Crystal parameters and X-ray diffraction data for Mn-$(NITpPy)_4[N(CN)_2]_2$

Chemical formula	$C_{52}H_{64}MnN_{18}O_8$
Formula weight	1124.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	17.768(7)
b/Å	7.368(4)
c/Å	21.404(8)
β/°	92.78(2)
V/Å^3	2799(2)
ρ (calc.)/g cm^{-3}	1.334
Z	2
μ/mm^{-1}	0.305
Reflections collected/unique	6983/6735
R_{int}	0.0795
R_1 $[I \geq 2\sigma(I)]^a$	0.0662
wR_2 $[I \geq 2\sigma(I)]^b$	0.1082

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2 Selected bond angles and distances for $Mn(NITpPy)_4$-$[N(CN)_2]_2$

Mn(1)···N(9)	2.204(4)	Mn(1)···N(8)	2.221(4)
Mn(1)–N(1)	2.277(3)		
N(7)–C(25)	1.295(6)	N(7)–C(26)	1.313(6)
N(8)–C(25)	1.131(6)	N(9)–C(26)^{I}	1.133(6)
N(2)–O(1)	1.274(4)	N(2)–C(6)	1.355(5)
N(3)–C(6)	1.318(5)	N(3)–O(2)	1.271(4)
N(5)–O(3)	1.282(4)	N(5)–C(18)	1.338(5)
N(6)–C(18)	1.339(5)	N(6)–O(4)	1.266(4)
N(9)–Mn(1)–N(8)	89.02(13)	N(9)–Mn(1)–N(1)	90.53(14)
N(8)–Mn(1)–N(1)	91.46(13)	N(8)–C(25)–N(7)	173.9(5)
N(9)^{II}–C(26)–N(7)	176.3(5)	C(25)–N(7)–C(26)	119.4(3)
C(25)–N(8)–Mn(1)	155.4(4)	C(26)^{I}–N(9)–Mn(1)	161.0(4)
O(1)–N(2)–C(6)	126.6(3)	O(1)–N(2)–C(7)	122.6(3)
C(6)–N(2)–C(7)	110.7(4)	O(2)–N(3)–C(6)	127.3(4)
O(2)–N(3)–C(8)	119.1(3)	C(6)–N(3)–C(8)	113.2(4)
N(3)–C(6)–N(2)	108.2(4)		
O(3)–N(5)–C(18)	126.7(4)	O(3)–N(5)–C(19)	119.7(3)
C(18)–N(5)–C(19)	113.5(4)	O(4)–N(6)–C(18)	126.5(3)
O(4)–N(6)–C(20)	120.8(4)	C(18)–N(6)–C(20)	112.4(3)
N(6)–C(18)–N(5)	108.8(4)		

Symmetry transformations used to generate equivalent atoms: I x, $y + 1$, z; II x, $y - 1$, z.

SHELXS-97[23] and refined with SHELXL-97[23] programs by full matrix least squares methods, on F^2. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride.

CCDC reference number 186/1756.

See http://www.rsc.org/suppdata/a9/a908891a/ for crystallographic files in .cif format.

Magnetic and spectroscopic measurements

IR characterizations were performed on a KBr pellet sample with an IR Bomem-Michelson 100 spectrometer. Magnetic studies were carried out on a powder sample enclosed in a medical capsule. Magnetic susceptibility measurements were performed at 0.1 T after zero field cooling, in the temperature range 2–300 K with a SQUID magnetometer SHE-VTS 906. Magnetization measurements were made at 2 K in the magnetic field range 0–4 T.

Results and discussion

Crystal structure

Selected bond distances and bond angles are summarized in Table 2. An ORTEP[29] drawing of the molecular structure is shown in Fig. 1. The crystal structure (Fig. 2) contains a mixed stack of coordinated and uncoordinated NITpPy units which are packed alternatively in the b direction. Fig. 3 shows a side view of one infinite 1-D stack in which the pyridyl rings of adjacent radicals are separated by 3.68 Å. The Mn atom is bonded to two apical NITpPy units and four equatorial $N(CN)_2$ units which bridge adjacent metal sites along the b axis. This arrangement is close to that observed in $Cu(NITpPy)_2$-$[N(CN)_2]_2{\cdot}3CH_3CN$[24] which contains only coordinated radicals. The distorted octahedral metal site is located on an inversion center, therefore, both radicals and anions are in *trans* positions. Each Mn is bonded to NITpPy radicals through the N atom of the pyridyl rings with Mn–N bond lengths of 2.277(3) Å. The angle between the pyridyl ring and the nitroxide groups is 27.0(1)°. The anions act as μ-bridging ligands with Mn···N8 and Mn···N9 bond lengths equal to 2.221(4) and 2.204(4) Å, respectively. The N–Mn–N angles range from 88.54(13) to 91.46(13)°. $[N(CN)_2]^-$ has pseudo C_{2v} symmetry with average C–N and N≡C bond lengths of 1.304 Å and 1.132 Å, respectively, as commonly observed in $[N(CN)_2]^-$ anions.[4–16] The Mn–N≡C angles of 155.4(4) and 161.0(4)° deviate from linearity, while N–C≡N angles (mean value 175.1°) are linear. The angle between $Mn(NITpPy)_2$ units and the b direction is equal to 8.18(5)°. The shortest distance between successive Mn atoms is 7.368(4) Å. The shortest contact between nitroxide groups (O2–O3 = 3.587(6) Å) is established between one NITpPy manganese coordinated unit and an uncoordinated radical belonging to the same stack. The shortest distance between radicals from adjacent stacks in the a direction is O1–O1 = 3.904(3) Å (Fig. 2).

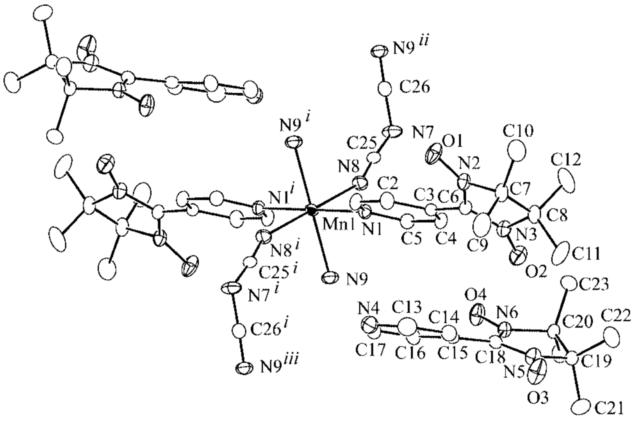


Fig. 1 ORTEP drawing with 20% ellipsoid probability showing atom labelling of $Mn^{II}(NITpPy)_4[N(CN)_2]_2$. Symmetry transformations used to generate equivalent atoms: *i*: $-x$, $1 - y$, $-z$; *ii*: x, $y - 1$, z; *iii*: $-x$, $2 - y$, $-z$.

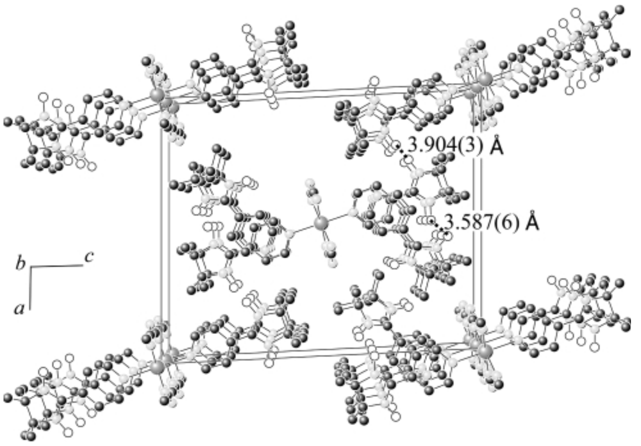


Fig. 2 Projection of the crystal structure in the ac plane showing packing of mixed stacks of coordinated and uncoordinated NITpPy units. The intermolecular distances O1–O1 = 3.904(3) Å and O2–O3 = 3.587(6) Å are shown.

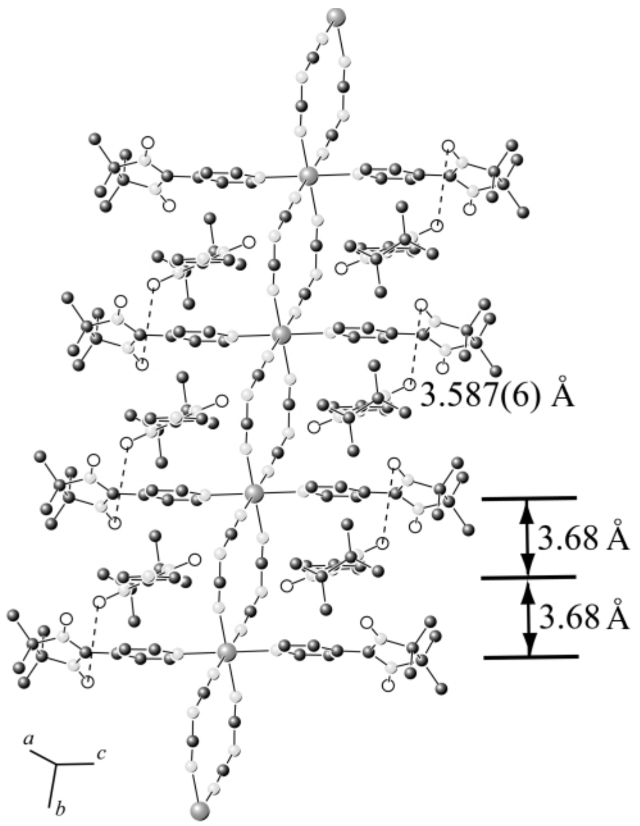


Fig. 3 Side view of the infinite 1-D chain generated from $Mn(NITpPy)_2$ units linked by $[N(CN)_2]_2$ μ-bridging ligands.

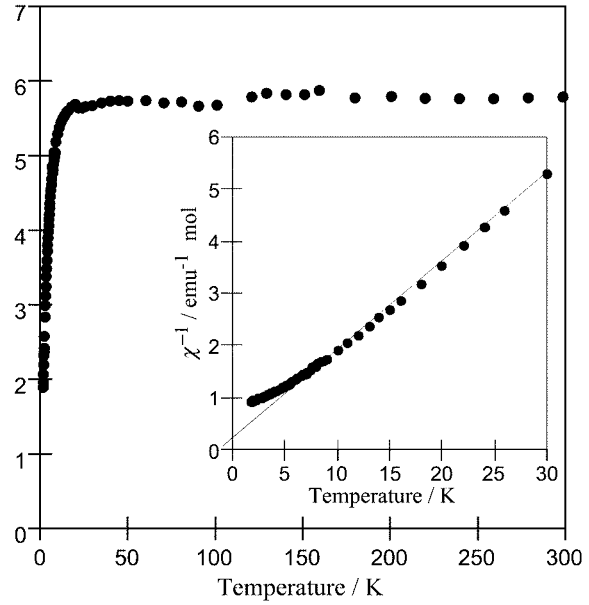


Fig. 4 $\chi_M T$ product as a function of temperature for the $Mn^{II}(NITpPy)_4[N(CN)_2]_2$ compound. Measurements performed under 0.1 T. Inset: χ_M^{-1} plot *vs*. temperature.

Magnetic properties

The molar susceptibility was corrected from the sample holder and diamagnetic contributions of all atoms by using Pascal's tables.[25] The molar susceptibility measured under 0.1 T, in the temperature range 2–300 K, obeys a Curie–Weiss law $\chi = C/(T - \theta)$ with an almost zero value of the Weiss constant θ (−0.7 K). The variation of $\chi_M T$ *versus* T is plotted in Fig. 4. The $\chi_M T$ value of 5.80 emu mol^{-1} K observed between 10 K and room temperature corresponds to what is expected (5.87 emu mol^{-1} K) for non interacting spins (one $S_{Mn} = 5/2$ and four $S_{Rad} = 1/2$). This value corresponds to an effective moment of 6.81 μ_B (μ_{th} (theoretical μ) = 6.85 μ_B). Below 10 K, the susceptibility data deviate from a Curie Law (see inset Fig. 4) suggesting the existence of weak antiferromagnetic interactions in this compound as indicated by the abrupt decrease of the $\chi_M T$ product. The magnetization measured at 2 K, shows a quite linear behaviour from 0 up to ≈2.5 T; the magnetic moment did not saturate under our experimental conditions and reached a value of 6.71 μ_B at 4 T, that is about 75% of the expected saturation moment (9 μ_B). The problem we are faced with is to identify the origin of the weak antiferromagnetic interaction. *A priori*, there are three possibilities of interaction, namely: (i) Mn(II)–coordinated NITpPy, (ii) coordinated NITpPy–noncoordinated NITpPy, (iii) Mn(II)–Mn(II) through the $N(CN)_2^-$ bridge. It is well established that the spin density on the nitrogen atom of the NITpPy pyridine ring is negligibly small. Therefore, the interaction between the Mn(II) ion and the coordinated radical should be negligibly small as well. The shortest O–O separation between coordinated and noncoordinated radicals is equal to 3.59 Å, which should also lead to a very weak interaction,[26–28] with a J parameter smaller than 0.1 cm^{-1} in absolute value. Such an intermolecular interaction cannot explain the profile of the curve of Fig. 4. On the other hand, the capability for $N(CN)_2^-$ to play the role of magnetic coupler is now well documented; some three dimensional dicyanamide-bridged compounds exhibit a long-range magnetic ordering.[4,8] Most likely, the low temperature magnetic behaviour arises from the weak antiferromagnetic coupling between Mn(II) ions through the dicyanamide bridge.

Conclusion

The *in situ* reaction of Mn^{2+}, NITpPy and $[N(CN)_2]^-$ yielded a one dimensional compound formulated as $Mn^{II}(NITpPy)_4[N(CN)_2]_2$ and containing columns of $[Mn^{II}(NITpPy)_2]^{2+}$ units linked by $N(CN)_2^-$ μ-bridging ligands. In the columns, the coordinated radicals alternate with uncoordinated ones in the *b* direction. While building such polymeric materials is achieved, magnetic interactions are not observed in this compound probably for structural reasons which reveal large distances between spin carriers. In order to build materials with higher dimensionality and magnetic interactions, we are investigating related compounds by using other paramagnetic metals (Cu^{II}, Co^{II}) and also other bridging ligands such as $C(CN)_3^-$ and paramagnetic hexacyanometallates $M(CN)_6^{3-}$, M = Fe^{3+}, Cr^{3+}.

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