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An Influence of Fluorinated Alkyl Substituents on Structure and Magnetic Properties of Mn(II) Complexes with Pyrazolyl-Substituted Nitronyl Nitroxides

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Abstract: New complexes of manganese(II) hexafluoroacetylacetonate [Mn(hfac)₂] with 2-(1-*R*-3-pyrazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl (*R* = CHF₂, CH₂CH₂F, CH₂CHF₂ or CH₂CF₃) were synthesised and characterised structurally and magnetically. All complexes were prepared under similar conditions. Nonetheless, their crystal structures were considerably different. Depending on the structure of fluorinated alkyl substituent *R*, the complexation reaction led to complexes of three types: chain-polymeric complexes with the head-to-head or head-to-tail motif and complexes of molecular structure. All complexes show strong antiferromagnetic behaviour in a high-temperature region (150–300 K) and weak ferro- or antiferromagnetic exchange interactions at low temperatures. The stronger antiferromagnetic exchange, -101.7 ± 1.5 or -136 ± 10 cm^{−1}, -82.3 ± 1.3 cm^{−1} and -87.4 ± 1.3 cm^{−1}, was attributed to the magnetic interaction in three- or two-spin clusters: $\{>N\cdots O-Mn^{2+}\cdots O\cdots N<\}$ or $\{>N\cdots O-Mn^{2+}\}$, respectively. The weaker antiferromagnetic interaction, -0.005 , between three-spin clusters or ferromagnetic interactions, $0.18\text{--}0.81$ cm^{−1}, between two-spin clusters are realised through the pyrazole ring or intermolecular contacts.

Keywords: nitronyl nitroxides; metal–nitroxide complexes; crystal structures; magnetic properties



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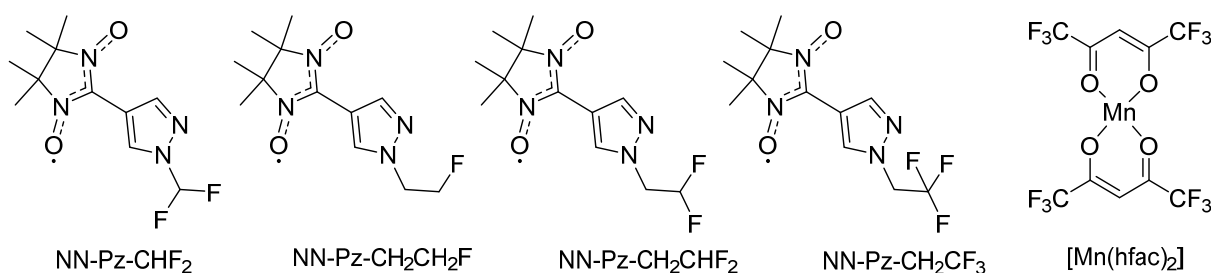
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1. Introduction

Nitroxide radicals have been proved to be promising ligands for the construction of molecular magnetic materials [1–3]. The ease of modification of nitronyl nitroxide radicals gives versatility to the design of various interesting systems of the metal–nitroxide type. Such systems have a large variety of topological structures and manifest intriguing bulk and molecular magnetic properties [4–6]. The direct linking of nitronyl nitroxides to metal ions results in the strongest possible magnetic coupling, which may reduce quantum tunnelling of the magnetisation and give a long relaxation time [7]. So far, a number of molecular magnets based on metal–nitroxide complexes have been created, for example, cobalt-radical coordination magnets with high coercivity blocking temperature [8,9]. In addition, discrete complexes with defined geometric structures of paramagnetic metal ions and nitronyl nitroxide radical ligands are good candidates for basic research on magneto-structural correlations [10–13].

In a preceding paper, we investigated the influence of step-by-step fluorination of different paramagnetic systems on their structure and magnetism [14–16]. The motivation was that the introduction of fluorine atom(s) into molecules alters physical and chemical properties of the compounds because of fluorine's electronegativity, its low polarisability and high bond strength [17]. In addition, there are many examples of the influence of substitution with fluorine on inter-molecular interactions and the use of 'organic fluorine' in crystal engineering or in the systematic design of functional materials [18–20]. Many research groups have performed comprehensive analyses of crystal structures of fluorine-containing compounds and published excellent reviews on the specific role of fluorine in crystal packing [21]. In some reviews, fluorine has been poetically described as the odd man out [22], the little atom that could [17], the atom with many faces [23], and the chameleon of noncovalent interactions [24]. Although there is ample research on inter-molecular interactions of the C–F group in various types of compounds, this kind of interaction has not been studied in a systematic series of complexes of paramagnetic metal ions with radicals. Intuitively, it is expected that the introduction of fluorine into metal–radical systems can have a significant influence on their packing in the crystals, thereby changing the inter-molecular exchange interaction channels and eventually magnetic characteristics of molecular magnetic materials.

Herein, we used a series pyrazolyl-substituted nitronyl nitroxides bearing different fluorinated alkyl groups in the pyrazole nucleus, namely 2-(1-*R*-3-pyrazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl, where *R* = CHF₂, CH₂CH₂F, CH₂CHF₂ or CH₂CF₃ (Scheme 1). The complexation reaction of [Mn(hfac)₂] with these radicals under identical conditions led to the formation of complexes of dimer structure, head-to-head chain-polymeric structure or head-to-tail chain-polymeric structure depending on the structure of the fluorinated alkyl substituent. Magnetic analyses showed that there is a strong antiferromagnetic interaction between the Mn(II) ion and the directly coordinated N–O group in the high-temperature region and weak ferro- or antiferromagnetic exchange interactions below 100 K.



Scheme 1. Ligands and [Mn(hfac)₂] acceptor matrix used for preparation of complexes 1–4.

2. Materials and Methods

2.1. General Procedures and Materials

First, 2-(1-*R*-3-pyrazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyls (L^R), where *R* = CHF₂, CH₂CH₂F, CH₂CHF₂ or CH₂CF₃, were synthesised according to methods from the literature [14]. All other chemicals were of reagent grade and used without purification. Toluene was distilled under an argon stream and kept in an argon atmosphere. Other solvents were of reagent quality and used without additional purification. IR spectra were obtained from KBr pellets by means of a Bruker VECTOR 22 infrared spectrometer. Elemental analyses for C, H and N were carried out using Perkin-Elmer elemental analyzer model 240.

2.2. Synthesis of Complex 1

A solution of 42 mg (0.08 mmol) of Mn(hfac)₂·2H₂O in 5 mL of dry toluene was heated under reflux for 40 min. After that, the solution was cooled to the room temperature, and a solution of NN-Pz-CHF₂ (22 mg, 0.08 mmol) in 1 mL of toluene was added. The resulting mixture was allowed to stand at −15 °C for a week to obtain blue blocks of crystals (30.9 mg,

57.5%). Anal. calcd. for $C_{21}H_{17}F_{14}MnN_4O_6$: C, 33.98; H, 2.31; N, 7.55. Found: C, 33.99; H, 2.20; N, 7.57%. IR (KBr, cm^{-1}): 3149(m), 2997(m), 2947(w), 1645(s), 1611(m), 1562(m), 1536(m), 1501(s), 1488(s), 1466(m), 1407(m), 1395(m), 1381(m), 1348(s), 1328(s), 1260(s), 1223(s), 1142(s), 1099(s), 1020(m), 1002(w), 965(w), 946(w), 892(m), 869(m), 838(s), 807(s), 766(w), 742(m), 697(w), 666(s), 609(w), 585(m), 542(m), 528(w), 483(w), 470(w), 419(w).

2.3. Synthesis of Complex 2

A solution of 42 mg (0.08 mmol) of $Mn(hfac)_2 \cdot 2H_2O$ in 5 mL of dry toluene was heated under reflux for 40 min. Next, the solution was cooled to room temperature, and a solution of NN-Pz- CH_2CH_2F (22 mg, 0.08 mmol) in 1 mL of toluene was introduced. The resulting mixture was kept at $-15^\circ C$ for several days to obtain blue blocks of crystals (32.2 mg, 52.4% based on Mn ion). Anal. calcd. for $C_{22}H_{20}F_{13}MnN_4O_6$: C, 35.79; H, 2.73; N, 7.59. Found: C, 35.52; H, 2.71; N, 7.81%. IR (KBr, cm^{-1}): 3153(m), 2996(w), 1649(s), 1610(w), 1556(w), 1530(m), 1500(m), 1350(m), 1301(w), 1257(s), 1206(s), 1146(s), 1097(w), 1039(w), 1019(w), 884(w), 863(w), 798(m), 758(w), 741(w), 665(m), 584(m), 544(w), 527(w), 507(w), 464(w), 435(w).

2.4. Synthesis of Complexes 3· C_7H_8 and 3

A solution of 42 mg (0.08 mmol) of $Mn(hfac)_2 \cdot 2H_2O$ in 5 mL of dry toluene was heated under reflux for 40 min. Then, the solution was cooled to room temperature, and a solution of NN-Pz- CH_2CHF_2 23 mg (0.08 mmol) in 1 mL of toluene was added. The resultant mixture was incubated at $-15^\circ C$ for ~20 h to obtain blue blocks of crystals of solvate complex 3· C_7H_8 . The crystals were filtered off and dried on air. Yield 40.9 mg (60.2%). The complex 3· C_7H_8 was stored for a month in vial at ambient condition that led to its desolvation. Anal. calcd. for $C_{22}H_{19}F_{14}MnN_4O_6$: C, 34.94; H, 2.53; N, 7.41. Found: C, 34.78; H, 2.60; N, 8.18%. IR (KBr, cm^{-1}): 3152(m), 2996(w), 2948(w), 1646(s), 1611(m), 1559(m), 1532(s), 1501(s), 1401(w), 1353(s), 1373 sh, 1320(w), 1303(w), 1259(s), 1214(s), 1192 sh, 1144(s), 1090(s), 1069(m), 1019(w), 1007(w), 946(w), 886(w), 867(w), 798(m), 742(w), 666(s), 642(w), 605(w), 585(m), 558(w), 544(w), 527(w), 484(w), 469(w), 436(w).

2.5. Synthesis of Complex 4· C_7H_8

A solution of 34 mg (0.07 mmol) of $Mn(hfac)_2 \cdot 2H_2O$ in 5 mL of dry toluene was heated under reflux for 40 min. After that, the solution was cooled to room temperature, and a solution of NN-Pz- CH_2CF_3 22 mg (0.07 mmol) in 3 mL of toluene was added. This mixture was allowed to stand at $-15^\circ C$ for ~24 h to obtain blue blocks of crystals (44.5 mg, 76.3%). Anal. calcd. for $C_{44}H_{36}F_{30}Mn_2N_8O_{12} \cdot 2(C_7H_8)$: C, 40.20; H, 3.02; N, 6.47. Found: C, 40.12; H, 3.01; N, 6.31%. IR (KBr, cm^{-1}): 3153(m), 3024(w), 2996(w), 2948(w), 1647(s), 1610(m), 1558(m), 1532(m), 1501(s), 1481 sh, 1438 sh, 1400(w), 1356(m), 1315(m), 1257(s), 1197(s), 1146(s), 1096 sh, 1020(m), 933(m), 889(w), 868(w), 841(w), 800(m), 766(w), 742(w), 664(m), 584(m), 542(w), 469(w), 433(w).

2.6. X-ray Crystallography Details

X-ray diffraction (XRD) data on monocrystals of 1, 2, 3· C_7H_8 and 4· C_7H_8 were collected at 100 K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω -scan technique) using mono-chromatised Cu K_α -radiation. The intensity data were integrated and corrected for absorption and decay in the CrysAlisPro software [25]. XRD data on monocrystals of 3 and $[Mn(hfac)_2(NN-Pz-CH_2CHF_2)]_n \cdot n[Mn(hfac)_2(NN-Pz-CH_2CHF_2)H_2O]$ were collected at 100 K on a Bruker D8 QUEST diffractometer. Single-crystal X-ray analyses were carried out in the APEX3 software [26]. Data reduction and integration were performed with Bruker-supplied software [27]. SADABS was used for scaling, empirical absorption corrections and for generating data files for structure solution and refinement [28]. The structures were solved by direct methods using SHELXT [29] and refined on F^2 with the help of SHELXL [30] in OLEX2 [31]. All non-hydrogen atoms were refined with individual anisotropic displace-

ment parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied to methyl groups.

CCDC 2272057 (for 1), 2272056 (for 2), 2239233 (for 3), 2239234 (for $[\text{Mn}(\text{hfac})_2(\text{NN-Pz-CH}_2\text{CHF}_2)]_n$), 2272055 (for $3 \cdot \text{C}_7\text{H}_8$) and 2272058 (for $4 \cdot \text{C}_7\text{H}_8$) contain the supplementary crystallographic data for the manganese–nitroxide complexes.

2.7. Magnetic Measurements

The variable-temperature magnetic-susceptibility measurements were carried out in the temperature range 2–300 K with a Quantum Design PPMS-9 or Quantum Design MPMSXL SQUID magnetometer. None of the complexes showed any field dependence of molar magnetic susceptibility at low temperatures. The molar magnetic susceptibility was corrected for the sample holder and diamagnetic contributions of all constituent atoms by means of Pascal's constants [32]. Analysis of the experimental magnetic data was performed using PHI program [33].

3. Results and Discussion

3.1. Synthesis and Crystal Structures of Manganese–Nitroxide Complexes

Complexes 1, 2, $3 \cdot \text{C}_7\text{H}_8$, 3, and $4 \cdot \text{C}_7\text{H}_8$ were prepared by interaction of manganese(II) hexafluoroacetylacetonate ($[\text{Mn}(\text{hfac})_2]$) with nitronyl nitroxides (NNs), namely 2-(1-*R*-3-pyrazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyls ($R = \text{CHF}_2$, $\text{CH}_2\text{CH}_2\text{F}$, CH_2CHF_2 or CH_2CF_3), in dry toluene at -15°C . The single-crystal X-ray analysis revealed that compound 1 crystallises in orthorhombic space group $I2/a$. The structure of 1 consists of 1D coordination chains as shown in Figure 1a. One can see that the paramagnetic NN-Pz- CHF_2 is a bridging bidentate ligand coordinated via the oxygen atom of one of the N–O groups and the nitrogen atom of the pyrazole ring. The coordination chains have a ‘head-to-head’ motif, and the nitroxide oxygen atoms and the nitrogen atom are coordinated to Mn in a *trans*-configuration. Each manganese ion is sixfold coordinated and has almost isometric octahedral geometry. For the MnO_6 unit, the Mn– O_{NO} bond lengths are 2.143 Å, whereas the average Mn– O_{hfac} bond length is 2.139 Å. These values are close to those observed for other complexes of $[\text{Mn}(\text{hfac})_2]$ with nitronyl nitroxides [34,35]. For the MnO_4N_2 unit, the Mn–N bond lengths are 2.297 Å, whereas the Mn– O_{hfac} bond lengths are 2.132 and 2.138 Å. In the coordinated nitroxide group, the bond length [1.303(2) Å] is slightly elongated as compared with the non-coordinated one [1.273(2) Å]. The crystal structure analysis of 1 shows that there are only two types of short inter-chain contacts, C–H... O_{NO} (2.539 Å) and C–H...F (2.396 Å), between the O atoms of nitronyl nitroxide moieties or the F atoms of the hfac ligands and H atoms of the methyl groups of the radical moieties (Figure S1.7). The shortest inter-chain distances between O atoms of the nitroxide groups exceed 5 Å (the sum of van der Waals radii of O atoms is 3.04 Å); this arrangement allows one to expect only very weak exchange interactions between the chains.

Figure 1b shows a schematic diagram of possible magnetic interactions within the manganese–nitroxide chains; the direct coordination bonding of two O atoms to Mn(II) should give the largest exchange interaction, which is denoted as J_1 , whereas magnetic couplings between Mn(II) ions and the nitroxide group via the pyrazole ring (denoted as J_2) should be weaker than J_1 . The sign and magnitude of these interactions are discussed in the Magnetic Properties section.

Complex 2 was found to crystallise in a monoclinic crystal system with space group $P2_1/c$. The structure of 2 also consists of 1D coordination chains (Figure 2) formed by bridging bidentate ligand coordination via the nitroxide O atom and the N atom of the pyrazole ring. As opposed to 1, the coordination chains have a head-to-tail motif, and the nitroxide O atom and N atom are coordinated to Mn in a *cis*-configuration. The coordination polyhedron of manganese is nearly isometric. The Mn– O_{NO} bond length is 2.145(2) Å, the Mn–N bond length is 2.236(2) Å, whereas the Mn– O_{hfac} bond lengths are 2.130(2), 2.144(2), 2.172(2) and 2.176(2) Å. In the coordinated nitroxide group, the bond length (1.305(3) Å) is

slightly elongated as compared with the non-coordinated one (1.278(3) Å). In solid 2, there are short inter-chain contacts, C–H⋯O_{NO} (2.665 Å) and C–H⋯F (2.577 Å), between the O atoms of nitronyl nitroxide moieties or the F atoms of the hfac ligands and H atoms of the methyl groups of the radical moieties (Figure S1.8). The shortest inter-chain distance between the oxygen atoms of nitroxide groups is 4.266 Å (Figure S1.8), which is also considerably greater than the sum of the van der Waals radii of O atoms (3.04 Å).

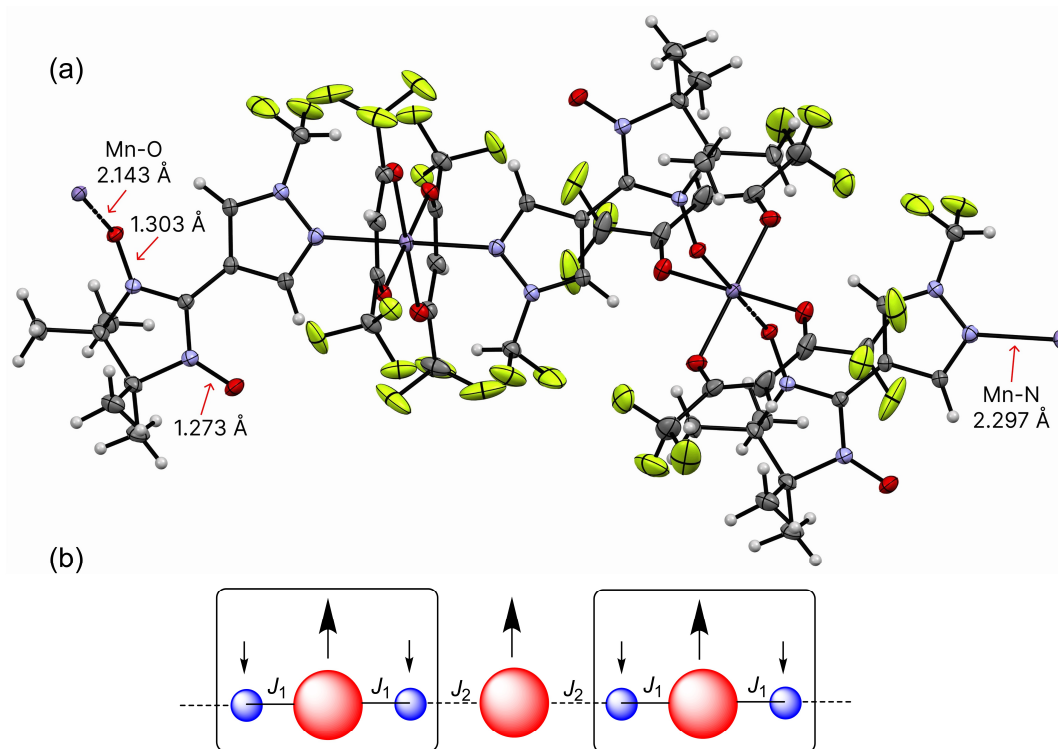


Figure 1. (a) View of a fragment of the chain in 1 with selected bond lengths (colour code: Mn: violet, N: blue, O: red, F: yellow, C: gray). Hereinafter, thermal ellipsoids are drawn with 50% probability. (b) Magnetic exchange pathways within and between the repeating units (the red and blue balls denote the $S_{\text{Mn}} = 5/2$ and $S_{\text{R}} = 1/2$ spins, respectively; the arrows indicate the spin alignment in the ground state).

The interaction of [Mn(hfac)₂] with NN-Pz-CH₂CHF₂ in dry toluene at −15 °C gave rise to complex 3·C₇H₈ in the form of a solvate with toluene. Complex 3·C₇H₈ was found to crystallise in the same monoclinic crystal system with space group $P2_1/n$. The structure of 3 also consists of 1D coordination chains (Figure 3) with the head-to-tail motif and *cis*-configuration of the Mn surroundings. The coordination of the manganese polyhedron is nearly isometric: the Mn–O_{NO} bond length is 2.138(3) Å, the Mn–N bond length is 2.245(3) Å whereas the Mn–O_{hfac} bond lengths lie in the range 2.126(2)–2.169(2) Å. In the coordinated nitroxide group, the bond length (1.309(4) Å) is slightly elongated as compared with the non-coordinated one (1.274(4) Å). The shortest inter-chain distances between the oxygen atoms of nitroxide groups exceed 5.0 Å (see Figure S1.9). After storage under ambient conditions, the complex 3·C₇H₈ loses the solvate molecules while retaining the quality of the crystals. According to XRD data, the crystal structure of desolvated complex 3 belongs to space group $P2_1/c$. In 3, geometric parameters are almost the same as in its solvate with toluene, for example, the Mn–O_{NO} bond length is 2.147(2) Å, and the Mn–N bond length is 2.247(2) Å, whereas the Mn–O_{hfac} bond lengths lie in the range 2.126(2)–2.178(2) Å. The N–O bond lengths are 1.310(3) and 1.277(3) Å for coordinated and non-coordinated nitroxide groups, respectively. The X-ray crystal structure analysis revealed that in 3 there are two types of short inter-chain contacts, C–H⋯O_{NO} (2.640 Å) and C–H⋯F (2.490 Å), between the O atoms of nitronyl nitroxide moieties or the F atoms

of the hfac ligands and H atoms of the methyl groups of the radical moieties. The shortest inter-chain distances between O atoms of the nitroxide groups exceed 4.5 Å (Figure S1.10).

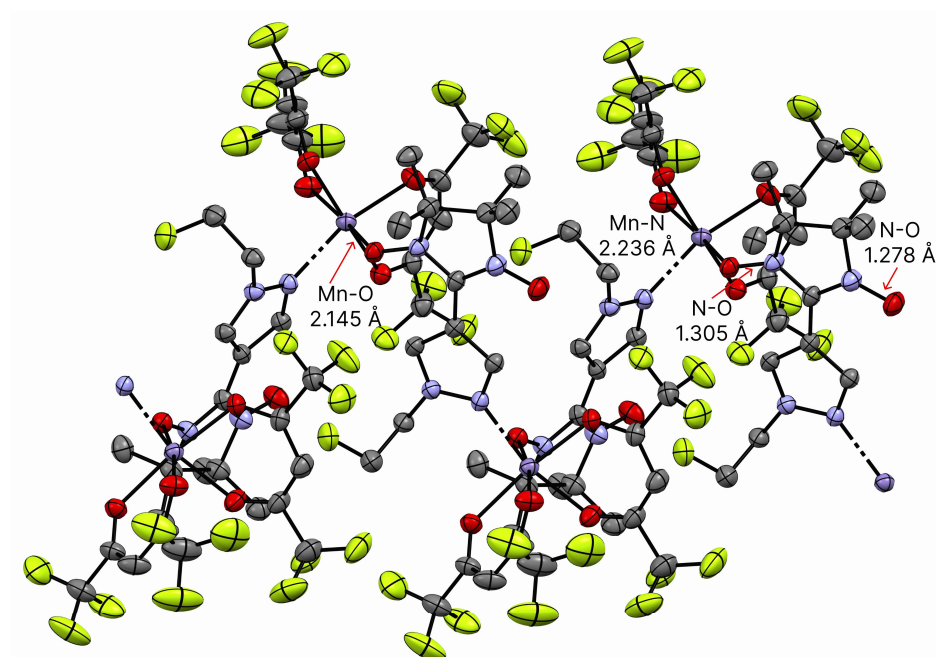


Figure 2. View of a fragment of the chain in **2** with selected bond lengths (colour code: Mn: violet, N: periwinkle, O: red, F: yellow, C: gray; H atoms are not shown for the sake of clarity).

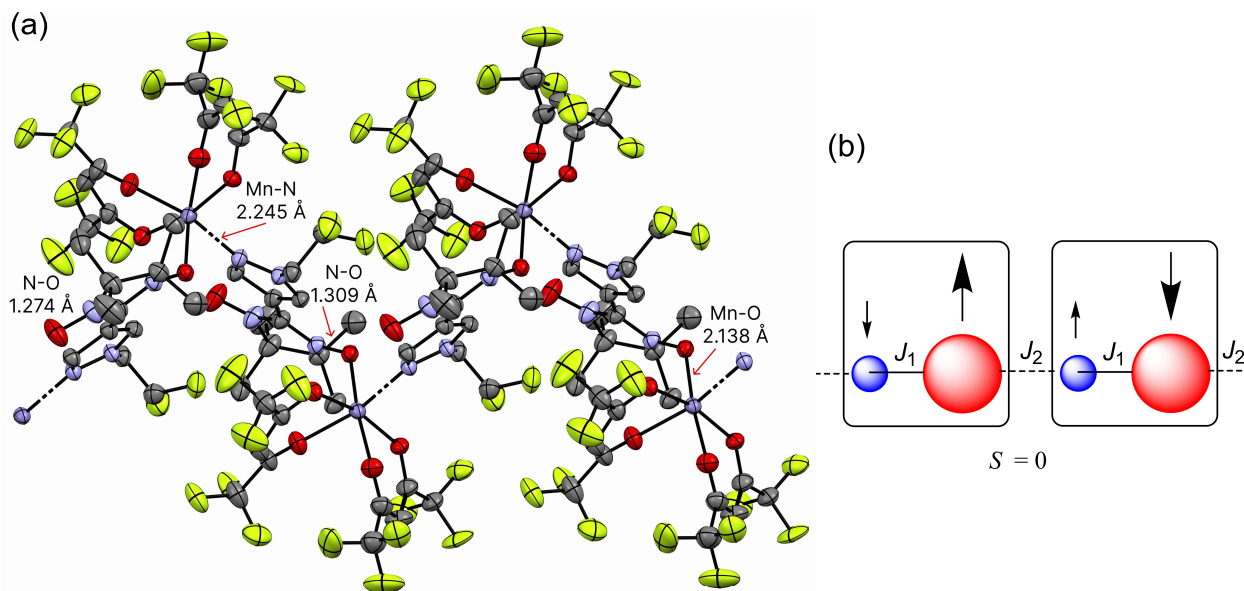


Figure 3. (a) View of a fragment of the chain in **3-C₇H₈** with selected bond lengths (colour code: Mn: violet, N: periwinkle, O: red, F: yellow, C: gray; the solvate molecules and H atoms are not shown). (b) Magnetic exchange pathways within and between the two spin clusters (the red and blue balls denote the $S_{\text{Mn}} = 5/2$ and $S_{\text{R}} = 1/2$ spins, respectively; the arrows indicate the spin alignment in the ground state).

In accordance with the structure of complexes **2** and **3**, there are two kinds of magnetic interactions in the chains: Mn(II)–nitroxide direct magnetic interactions, J_1 , and Mn(II)–nitroxide interactions through the pyrazole ring: J_2 (Figure 3b). It is known that nitroxide radicals directly bound to Mn(II) centres through the N–O group always exhibit much

stronger magnetic coupling than that through a donor atom of the nitronyl nitroxide substituent [36–38]. Therefore, from a magnetic point of view, the coordination chain can be described as strongly coupled two-spin clusters with a relatively weak exchange between them: J_2 . The quantification of these magnetic interactions is discussed in the Magnetic Properties section.

The reaction of $\text{Mn}(\text{hfac})_2$ with $\text{NN-Pz-CH}_2\text{CF}_3$ led to the formation solvate complex $4 \cdot \text{C}_7\text{H}_8$ having structure of a cyclic dimer (Figure 4). Crystal structure of the complex belongs to the triclinic crystal system with space group $P-1$. The structure of the complex results from the bridging bidentate ligand coordination via the nitroxide O atom and the N atom of the pyrazole ring. The Mn-O_{NO} bond length is 2.110(2) Å, and the Mn-N bond length is 2.278(2) Å, which are comparable to those observed in previously reported cyclic metal–nitroxide dimers [39–41]. In the coordinated nitroxide group, the bond length is also slightly elongated (1.303(2) Å) as compared with the non-coordinated one (1.272(3) Å). The $\text{Mn} \cdots \text{Mn}$ distance in the intra-dimer is 6.248 Å, which is shorter than the shortest inter-dimer $\text{Mn} \cdots \text{Mn}$ distance of 8.984 Å. The shortest distance between the uncoordinated NO groups is 4.886 Å. The packing diagram for $4 \cdot \text{C}_7\text{H}_8$ is shown in Figure S2. The cyclic dimers are arranged parallel to each other along the a -axis, thereby forming stacks, between which the shortest contacts that are established by oxygen atoms (O1) of the uncoordinated nitroxide groups and hydrogen atoms (H6C) of methyl groups are 2.532 Å (Figure S1.11). It is also noteworthy that unlike complex $3 \cdot \text{C}_7\text{H}_8$, solvate complex $4 \cdot \text{C}_7\text{H}_8$ is stable under ambient conditions and does not lose the solvent molecules.

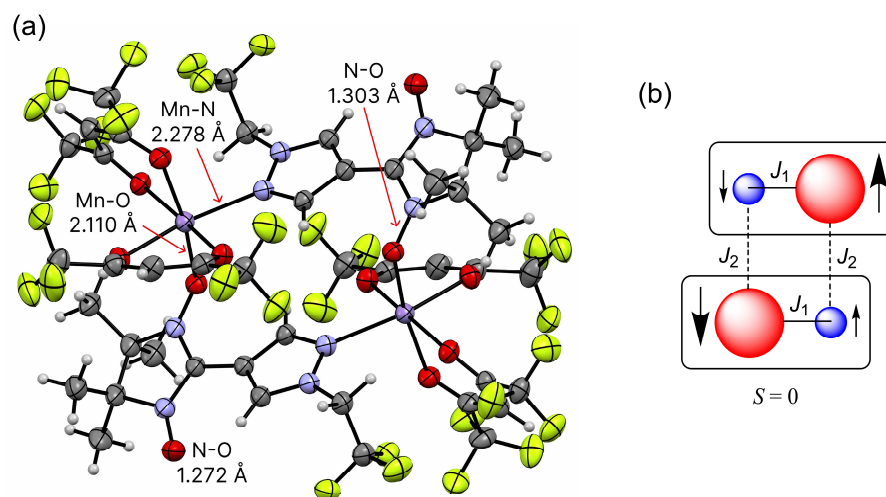


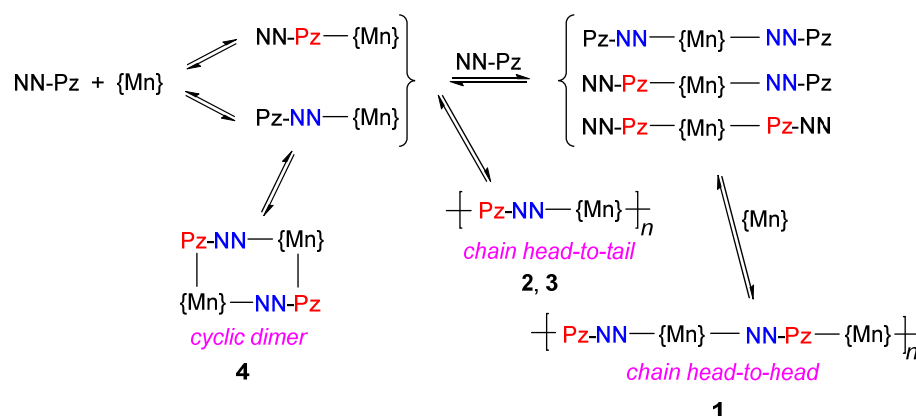
Figure 4. (a) View of a cyclic dimer in $4 \cdot \text{C}_7\text{H}_8$ with selected bond lengths (colour code: Mn: violet, N: periwinkle, O: red, F: yellow, C: grey; the solvate molecules are not shown). (b) Magnetic exchange pathways within the dimer (the red and blue balls represent the $S_{\text{Mn}} = 5/2$ and $S_{\text{R}} = 1/2$ spins, respectively; the arrows indicate the spin alignment in the ground state).

In **4**, there are mainly two kinds of magnetic interactions for the present four-spin magnetic system, i.e., the magnetic interaction between the Mn(II) ion and the directly coordinated nitroxide group (J_1) and the magnetic coupling between the Mn(II) ion and nitroxide group through the pyrazole rings (J_2) (Figure 4b). The second kind of magnetic coupling will be shown below to be weak and ferromagnetic (see the Magnetic Properties section).

The experimental powder XRD patterns of all complexes matched well the simulated XRD patterns based on the structures refined by single-crystal XRD analysis. In addition, elemental analyses yielded satisfactory results for all manganese–nitroxide complexes. The preparation of the complexes and their characterisation were repeated at least three times; the results (yields, crystal structures) were reproducible.

Notably, the reaction of $[\text{Mn}(\text{hfac})_2]$ with $\text{NN-Pz-R}^{\text{F}}$ under the same conditions produced complexes of different types: a chain-polymeric complex with a head-to-head motif

or head-to-tail motif as well as a molecular complex. The reason is a fine influence of fluorinated alkyl substituents R in NN-Pz on a set of equilibrium constants predetermining concentrations of different species and their solubility (Scheme 2). In NN-Pz-CH₂CF₃, the fluoroalkyl substituent somewhat reduces electron density on the donor nitrogen atom, and this effect obviously should favour the formation of a soluble Pz-NN-{Mn} complex with a coordinated NO group. If we assume that the acceptor ability of the manganese atom in Pz-NN-{Mn} is not sufficient to bind one more ligand, then the formation of a cyclic dimer with pairwise coordination bonds becomes preferable and therefore leads to precipitation of 4. Incidentally, the reasons may be the same for the frequent formation of such dimers during the interaction of [Mn(hfac)₂] with hetaryl-substituted nitronyl nitroxides [38,42–46].



Scheme 2. Plausible pathways to different Mn-nitroxide complexes.

On the contrary, only one case is known when the reaction of [Mn(hfac)₂] with a hetaryl-substituted nitronyl nitroxide produces a chain-polymeric complex, moreover, having a head-to-head motif [35]. In our case, the 1 complex has similar structure, and its formation can be explained by the influence of the CHF₂ substituent, which reduces electron density on the donor nitrogen atom to such an extent that the formation of the corresponding dimer becomes thermodynamically unfavourable. Therefore, the process goes further along the path of coordination of another radical by the manganese ion through the NO group with the formation of a three-spin molecule: Pz-NN-{Mn}-NN-Pz. The interaction of the latter with the [Mn(hfac)₂] acceptor matrix eventually gives a poorly soluble chain-polymeric complex with a head-to-head motif (Scheme 1). Incidentally, one can notice an interesting detail: only in this case does the complex precipitate into a solid phase very slowly (for approximately a week), whereas solid phases of the other complexes described here form much faster, within several hours. This finding indirectly indicates that the concentration of the Pz-NN-{Mn}-NN-Pz form that is necessary for the assembly of the solid phase of the 1 complex is too low in the solution.

The structure of the two remaining complexes, 2 and 3, is unprecedented. These are the first examples of manganese-nitroxide chain-polymeric complexes with a head-to-tail motif in which hetaryl-substituted nitronyl nitroxides serve as bidentate-bridging ligands. Their formation can be explained as follows: a decrease in electron acceptor properties of substituent R possibly enhances the donor ability of the nitrogen atom of the paramagnetic ligand to such an extent that the NN-Pz-{Mn} complex becomes preferable in the solution, thereby causing crystallisation of the chain head-to-tail complexes (Scheme 1).

The effect of R^F substituents on the course of the complexation reactions can also be observed visually. As mentioned above, the 1 complex precipitates very slowly, and after 24 h, one can see the emergence of a small amount of the product (Supplementary Materials Figure S1.1). In the case of 2, after 24 h under the same conditions, a gel-like product initially arises, retaining the entire mother liquor. This product, upon further incubation of the reaction mixture for several days, transitions to a crystalline 2 complex. The two latter complexes, 2 and 3, form faster and after 24 h almost completely precipitate with

the emergence of crystalline phases. Thus, the fluorinated substituents in NN-Pz have a substantial effect on the structure of heterospin manganese–nitroxide complexes. It is noteworthy that their solid phases have different sets of exchange channels, and therefore a difference in magnetic behaviour is expected.

3.2. Magnetic Properties

The temperature dependence of effective magnetic moment μ_{eff} for **1** is shown in Figure 5. The μ_{eff} value at 300 K is $5.17 \mu_{\text{B}}$ and slightly decreases to reach a plateau of $4.99 \mu_{\text{B}}$ in the temperature range 150–10 K. The observed μ_{eff} values in the temperature range 10–300 K are considerably less than the theoretical spin-only value of $6.16 \mu_{\text{B}}$ for the non-interacting spin system of Mn^{2+} and nitroxide based on the $\{\text{Mn}(\text{hfac})_2(\text{NN-Pz-CHF}_2)\}$ moiety. It is reasonable to explain the observed magnetic behaviour of **1** by the strong antiferromagnetic interactions in $\{>\text{N}=\text{O}-\text{Mn}^{2+}-\text{O}=\text{N}<\}$ three-spin exchange clusters, in which the spins of the coordinated N=O groups partially compensate the spin of the Mn^{2+} ion ($S_{\text{Mn}} = 5/2$). In the range from 150 to 10 K, the μ_{eff} values are close to theoretical value $\mu_{\text{teor}} = (0.5 \cdot 15 + 0.5 \cdot 35)^{1/2} = 5 \mu_{\text{B}}$, taking into account that the magnetic susceptibility contains contributions only from residual moments of the three-spin exchange clusters having a quartet ground state ($S = 3/2$) and from the moments of the Mn^{2+} ions located in MnO_4N_2 coordination units ($S_{\text{Mn}} = 5/2$). The decline of μ_{eff} below 10 K down to $4.69 \mu_{\text{B}}$ at 2 K is explained by the weak inter-chain antiferromagnetic interactions (Figure 1b). Analysis of the experimental $\mu_{\text{eff}}(T)$ dependence, using a trimer model for the $\{>\text{N}=\text{O}-\text{Mn}^{2+}-\text{O}=\text{N}<\}$ exchange cluster (spin-Hamiltonian $H = -2J(S_{R1}S_{Mn} + S_{Mn}S_{R2})$) while taking into account the magnetic susceptibility of the Mn^{2+} ions located in MnO_4N_2 coordination units according to Curie law, allows us to estimate exchange interaction energy. The weaker intercluster exchange interactions zJ' were taken into account in the mean field approximation. In the PHI program [33], the best fit values of g-factors and exchange interaction parameter J and zJ' are 2.01 ± 0.01 , $-101.7 \pm 1.5 \text{ cm}^{-1}$ and $-0.005 \pm 0.001 \text{ cm}^{-1}$, respectively.

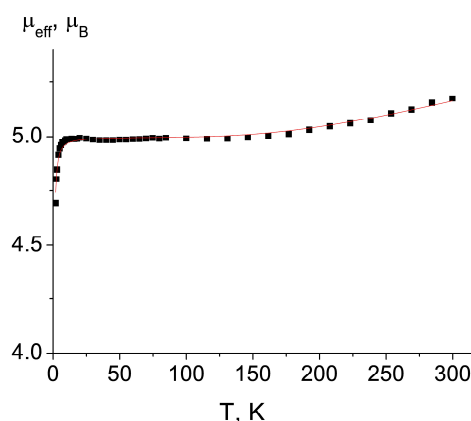


Figure 5. The temperature dependence of μ_{eff} for complex **1**. The solid curve corresponds to the best theoretical fit.

For complexes **2** and **3** with a head-to-tail motif of chains, the $\mu_{\text{eff}}(T)$ dependences are similar (Figure 6). The μ_{eff} values are 5.34 and $5.37 \mu_{\text{B}}$ and slightly decrease with diminishing temperature. The μ_{eff} values in the temperature range 300–50 K are close to the theoretical spin-only value of $4.90 \mu_{\text{B}}$ for one paramagnetic centre with $S = 2$, indicating the realisation of strong antiferromagnetic exchange interactions in $\{\text{Mn}^{2+}-\text{O}=\text{N}<\}$ exchange clusters. Below 50 K, μ_{eff} values drop rapidly, which is caused by the weak inter-cluster interactions within the chains. Analysis of the experimental $\mu_{\text{eff}}(T)$ dependences using a two-spin model (spin-Hamiltonian $H = -2J_1S_{Mn}S_R$) as reported in [47] enabled us to estimate the exchange interaction energy in $\{\text{Mn}^{2+}-\text{O}=\text{N}<\}$ exchange clusters. The weak intercluster exchange interactions J_2 (see Figure 3b) cause the decreasing of μ_{eff} at low temperatures. The best-fit values of g-factors and exchange interaction parameters J_1

and J_2 are 2.029 ± 0.003 , $-136 \pm 10 \text{ cm}^{-1}$ and $0.78 \pm 0.01 \text{ cm}^{-1}$ for 2, and 2.041 ± 0.002 , $-82.3 \pm 1.3 \text{ cm}^{-1}$ and $0.18 \pm 0.01 \text{ cm}^{-1}$, respectively, for 3. The small positive value of J_2 may be attributed to FM exchange between the Mn(II) ion and the nitronyl nitroxide moiety through the pyrazole ring.

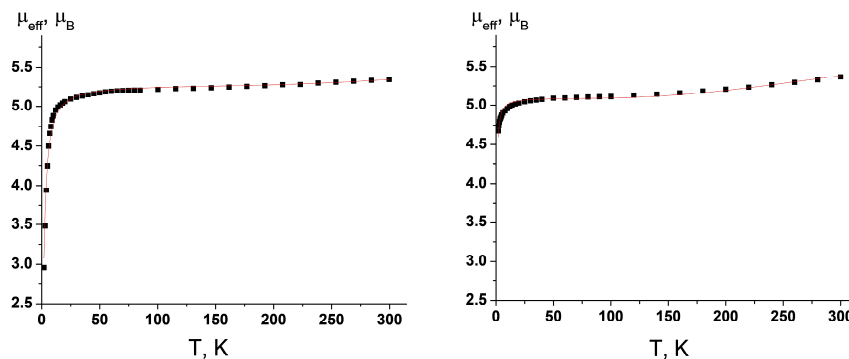


Figure 6. The $\mu_{\text{eff}}(T)$ dependencies for complexes 2 (left) and 3 (right). Solid curves are theoretical ones.

For cyclic dimer 4, the temperature dependence of μ_{eff} is presented in Figure 7a. The room temperature μ_{eff} value is approximately $7.52 \mu_{\text{B}}$. As the temperature is lowered, μ_{eff} slightly decreases, reaching a plateau of $7.20 \mu_{\text{B}}$ at 100 K and then drops rapidly at temperatures below 15 K. In the temperature range of plateau 30–100 K, the observed μ_{eff} values are considerably less than the theoretical spin-only value ($8.72 \mu_{\text{B}}$) for the non-interacting spin system of two Mn^{2+} ions and two nitroxide ligands based on the unit with the 4 formula. As in the previous complexes, the observed magnetic behaviour of 4 can be explained by the strong antiferromagnetic interactions in $\{\text{Mn}^{2+}\text{--O--N}<\}$ exchange clusters, in which the spins of the coordinated N–O groups are completely coupled to the two spins of Mn^{2+} . Therefore, the magnetic susceptibility has contributions only from the residual moments of two exchange clusters ($S = 2$) (the theoretical spin-only magnetic moment of $\mu_{\text{teor}} = 6.93 \mu_{\text{B}}$). The further decrease in μ_{eff} at $T < 10$ can be attributed to the weak interactions between two-spin $\{\text{Mn}^{2+}\text{--O--N}<\}$ exchange clusters. Analysis of the experimental $\mu_{\text{eff}}(T)$ dependencies with a tetramer model using spin-Hamiltonian $H = -2J_1(S_{\text{Mn}1}S_{\text{R}1} + S_{\text{Mn}2}S_{\text{R}2}) - 2J_2(S_{\text{Mn}1}S_{\text{R}2} + S_{\text{Mn}2}S_{\text{R}1})$ as reported in [46,48] gives the best fit values of g-factors and exchange interaction parameters J_1 and J_2 : 2.0036 ± 0.002 , $-87.4 \pm 1.3 \text{ cm}^{-1}$ and $0.81 \pm 0.01 \text{ cm}^{-1}$, respectively. Parameter J_1 corresponds to a strong antiferromagnetic exchange in the $\{\text{Mn}^{2+}\text{--O--N}<\}$ moieties, and J_2 corresponds to weak interactions between spins of the Mn^{2+} ion and the nitroxide coordinated via the N atom.

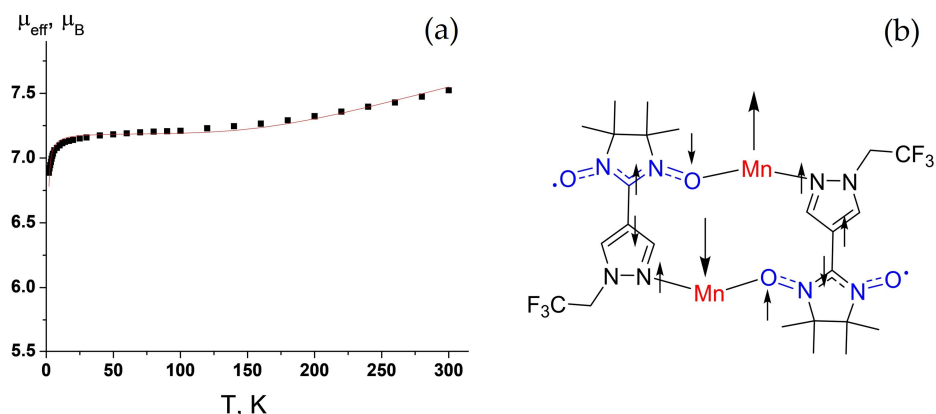


Figure 7. The $\mu_{\text{eff}}(T)$ dependencies for complex 4; the solid curve corresponds to the best theoretical fit (a). The spin polarisation mechanism for the intra-dimer magnetic coupling (b).

The strong antiferromagnetic interaction can be attributed to the effective overlap between the π -SOMO orbital containing the unpaired electrons of the nitronyl nitroxide moiety and d orbitals of the Mn(II) ion [49–52]. The experimental J_1 value in 4 has the same order of magnitude as that observed in different dimeric complexes (Table 1).

Table 1. Selected geometric parameters and experimental J_1 values in the dimer complex 4 and cousin dimeric complexes of Mn(hfac)₂ with nitronyl nitroxides.

Dimeric Complex	d(Mn–O), Å	∠Mn–O–N, °	J_1 Value, ^a cm ^{−1}	Ref.
[Mn(hfac) ₂ (NITpPy)] ₂	2.129(4)	123	−73	[53]
[Mn(hfac) ₂ (NIT–thien–3–Py)] ₂	2.156(3)	131	−74	[54]
[Mn(hfac) ₂ (QNXL–2NIT)] ₂	2.134(4)	125	−77	[46]
[Mn(hfac) ₂ (NIT–Ph–m–OCH ₂ trz)] ₂	2.068–2.083 ^b	123–127	−77	[45]
Complex 4	2.110(1)	124	−87	This work
[Mn(hfac) ₂ (4–NITPhPyrim)] ₂	2.148(5)	133	−88	[48]
[Mn(hfac) ₂ (NIT–3–Py)] ₂	2.115(4), 2.149(4) ^b	123, 121	−97	[37]
[Mn(hfac) ₂ (NITPhIm)] ₂	2.124(3)	125	−100	[43]
[Mn(hfac) ₂ (NIT–5–Pyrim)] ₂	2.130(2)	125	−103	[37]
[Mn(hfac) ₂ (p–PONIT)] ₂	2.142(3)	127	−109	[55]
[Mn(hfac) ₂ (NIT–3PyPh)] ₂	2.151(4)	123	−208	[38]
[Mn(hfac) ₂ (4–QNNN)] ₂	2.132(1)	129	n.d.	[41]

^a The spin Hamiltonian is defined as $H = -2J_1 S_{Mn} \cdot S_R$. ^b Two independent molecules.

The observed difference in antiferromagnetic coupling (from −74 to −208 cm^{−1}) may be ascribed to the different coordination geometry of the manganese–nitroxide spin cluster affecting the overlap of the magnetic orbitals. The small positive J_2 value shows that a weak ferromagnetic coupling exists between the two {Mn–O–N} moieties and is mediated by the pyrazole rings (Figure 7b), thus giving rise to the non-magnetic ground spin state. This weak ferromagnetic interaction can be explained by the spin polarization mechanism.

4. Conclusions

In summary, the complexation reaction of [Mn(hfac)₂] with pyrazolyl-substituted nitronyl nitroxides bearing various fluorinated alkyl groups (−CHF₂, −CH₂CH₂F, −CH₂CHF₂ or −CH₂CF₃) in the pyrazole core was investigated. The most interesting result of this investigation is that depending on the structure of the fluorinated alkyl substituent, the complexation reaction of [Mn(hfac)₂] with these radicals under identical conditions affords complexes of head-to-head chain-polymeric structure, head-to-tail chain-polymeric structure or molecular structure. In all complexes, nitronyl nitroxide ligands act as a bridging ligand linking Mn(II) ions through the O atom of the nitroxide group and the N atom of the pyrazole ring, thereby creating three-spin {>N–O–Mn²⁺–O–N<} or two-spin {Mn²⁺–O–N<} exchange clusters. According to magnetic measurements, in all the clusters, the Mn²⁺ ion strongly interacts antiferromagnetically with the coordinated nitroxide group. Our investigation shows that the structure of the metal–nitroxide complexes can be modulated by the step-by-step fluorination of the radical ligand, thus making it possible to obtain coordination compounds with a previously unknown motif. Further studies on magnetostructural correlations of related organic and inorganic composite systems are in progress.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13101528/s1>, Figure S1.1. Images of inverted reaction vessels with reaction mixtures [Mn(hfac)₂] + NN-Pz-CHF₂ and [Mn(hfac)₂] + NN-Pz-CH₂CH₂F after incubation at −15 °C for 24 h; Figures S1.2–S1.5: Fragments of crystal structures of complexes with shown cell axes; Figure S1.6: View of a fragment of the crystal structure of [Mn(hfac)₂(NN–Pz–CH₂CHF₂)]_n·n[Mn(hfac)₂(NN–Pz–CH₂CHF₂)H₂O]; Figures S1.7–S1.11: Short inter-chain and inter-molecular contacts; Figures S2.1–S2.5: Experimental and calculated powder X-ray diffrac-

tion pattern for 1, 2, 3·C₇H₈, 3, and 4·C₇H₈. Tables S1.1 and S1.2: Crystal data for complexes; Tables S1.3–S1.7: Selected bond distances in 1, 2, 3·C₇H₈, 3, and 4·C₇H₈.

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