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Pyrazol-4-yl-substituted α -nitronyl and α -imino nitroxide radicals in solution and solid states

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Abstract

The synthesis, solution studies, X-ray structures and magnetic properties of two new radical derived pyrazole ligands, based on α -nitronyl and imino nitroxides are reported. The spin distribution on the radicals has been studied in solution using EPR spectroscopy on dilute solutions. In concentrated solutions the radicals form aggregates in solution in which the magnetic interactions have been studied using low-temperature EPR spectroscopy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pyrazole; Hydrogen bonds; EPR spectroscopy; Magnetic interactions; Nitroxide

1. Introduction

Derivatives of pyrazole are interesting components for purely organic and metallo-organic molecular magnetic materials [1–3], because: (i) hydrogen bonds, a typical feature of these derivatives [4–7] (Fig. 1), are known to influence the transmission of magnetic interactions [8–18]; (ii) the inclusion of hetero-atoms in the ring can aid spin-delocalisation by spin-polarisation over the ring [19]; (iii) they “self-assemble” in solution [20], a facet that permits the study of magnetic interactions in well-defined aggregates; and (iv) they permit access to a variety of potentially-interesting metal ion complexes [21–27].

In the solid state, pyrazole derivatives adopt a variety of packing forms, from cyclic dimers, trimers [5] (Fig. 1) and even tetramers, to topologically linear chains (which take on a number of topographical guises, such as helices [4]), all of which involve the [N–H \cdots N] pyrazole hydrogen bond [7]. The α -nitronyl nitroxides derived from triazole (TzNN) [8] and imidazolyl (ImNN) [11–13] both exhibit extremely strong ferro- and antiferromagnetic interactions, respectively, for or-

ganic radicals in which the hydrogen bonds have been involucrated. In addition the pyrazoles and pyrazolates exhibit a rich coordination chemistry with metal ions

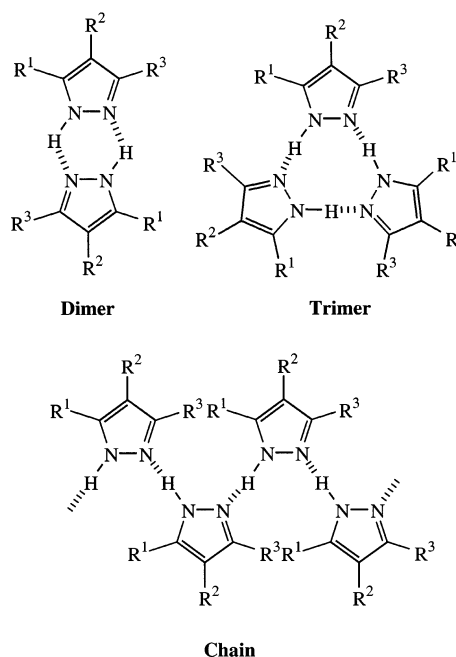


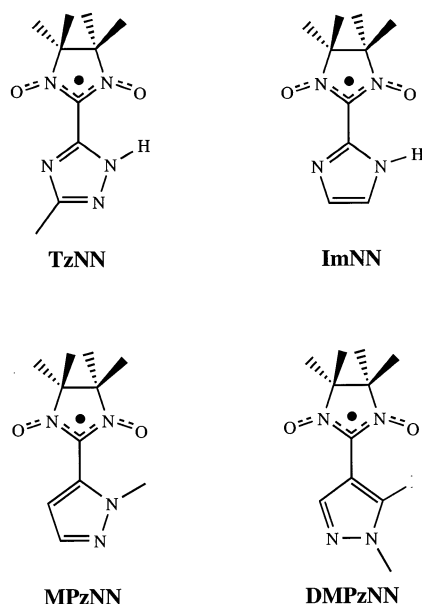
Fig. 1. Non-covalent aggregates formed by pyrazole derivatives in the solid state [7].

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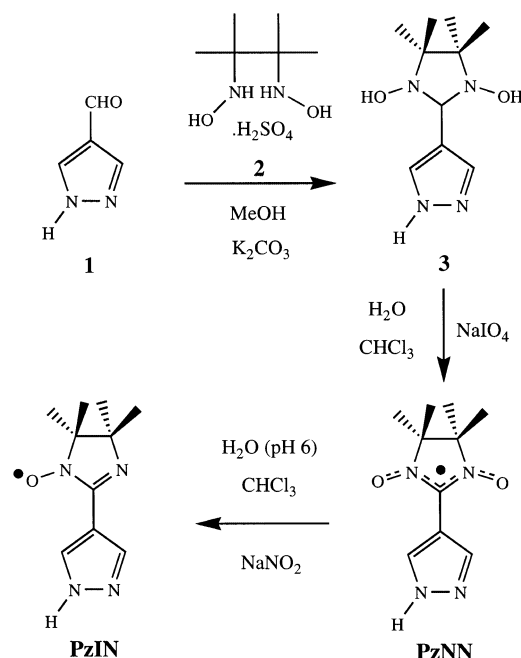
[21–27] in common with the nitronyl nitroxides, and their combination is an appealing one for augmenting the strength and dimensionality of the magnetic interactions within the materials.

With all these objectives in mind, we have prepared the persistent free radicals **PzNN** (pyrazol-4-yl-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-3-ium-1-oxyl) and **PzIN** (pyrazol-4-yl-4,4,5,5-tetramethyl-2-imidazolyl-3-oxyl) (Scheme 1) and have studied their aggregation behaviour in solution, the magnetic properties of these aggregates in solution, and the bulk magnetic properties of the molecular materials in the crystalline state, and report our results here. After we completed the synthesis of these compounds, Vasilevsky et al. [28] reported the synthesis and magnetic properties of some methylated pyrazolyl nitroxides, among them **MPzNN** and **DMPzNN**, in which there is no possibility of the formation of strong hydrogen bonds.



2. Results and discussion

The radical **PzNN** was synthesised (Scheme 1) using a slight modification of the classic route pioneered by Ullman and coworkers [29], by condensation of 4-formyl pyrazole **1** [30] with 2,3-bis(hydroxylammonium)-2,3-dimethylbutane sulfate (**2**) in the presence of potassium carbonate in methanol, followed by oxidation of the resulting isolated adduct **3** with NaIO_4 in a biphasic mixture of water and dichloromethane. After purification by column chromatography, the resulting blue oil was crystallised from a mixture of dichloromethane and hexane. The corresponding imino nitroxide radical **PzIN** was obtained (Scheme 1) by deoxygenation of **PzNN** in a biphasic mixture (chloroform/water) acidified to pH 6 and containing sodium



Scheme 1.

nitrite, [31] and was purified by chromatography on silica gel. Thin orange needles suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution of the radical.

The identity and purity of each compound was confirmed by elemental analysis, FT-IR spectroscopy, laser desorption/ionisation time-of-flight mass spectrometry (LDI-TOF MS), EPR spectroscopy and X-ray crystallography. The IR spectra of **PzNN** and **PzIN** show a symmetric stretching band of the NO group at 1367 and 1370 cm^{-1} , respectively, a normal position for this band and not indicative in itself of strong hydrogen bonds. The positive mode LDI-TOF mass spectrum of **PzNN** revealed peaks at 223 Da, corresponding to the molecular ion, as well as two other fragment ions corresponding to the loss of one and two oxygen atoms, respectively, from the α -nitronyl nitroxide ring. In the case of the radical **PzIN**, the sodium ion adduct of the molecular ion was observed.

As far as the X-band EPR spectra of the radicals are concerned, that of an aqueous solution of **PzNN** at room temperature consists of a five-line pattern as a result of the coupling of the unpaired electron with the two equivalent nitrogen nuclei of the α -nitronyl nitroxide ring. Moreover, magnetic coupling with the 12 hydrogens of the α -nitronyl nitroxide methyl groups, the three hydrogens and the two nitrogen nuclei of the pyrazolyl ring leads to further splitting of each of the five lines. Adding NaOH to the solution results in a simplified hyperfine fine structure (Fig. 2). In both cases the hyperfine coupling of the unpaired electron with the nitrogen atoms of the pyrazolyl ring could be resolved,

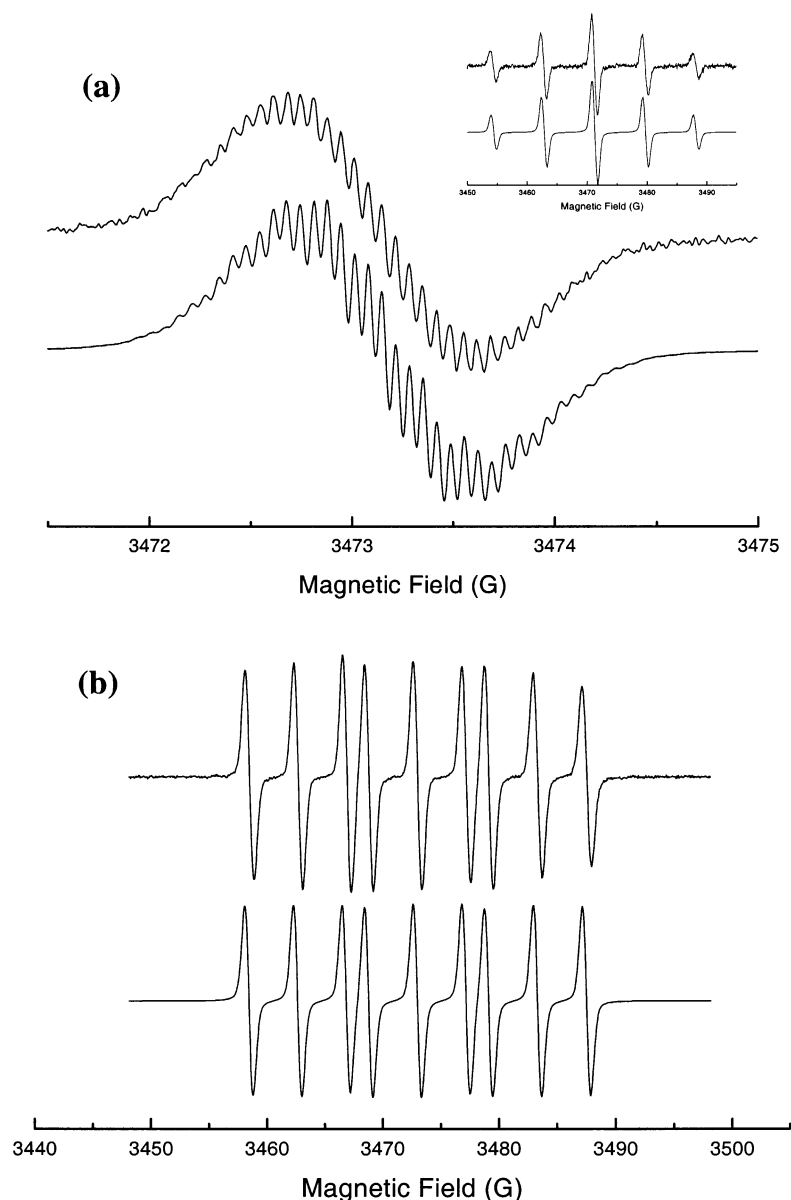


Fig. 2. Room temperature EPR spectrum of a dilute solution of NaOH/water and corresponding simulations of **PzNN** (a: central $M_1 = 0$ line and full spectrum in inset (top — experimental, bottom — simulated)) and **PzIN** (b: full spectrum (top — experimental, bottom — simulated)).

and is reported in Table 1. The small value of these hyperfine coupling constants indicates that a very small amount of spin density is present on these atoms.

The typical seven-line pattern observed for **PzIN** (coupling of the electron with two non-equivalent nitrogen atoms of the α -imino nitroxide) in toluene/dichloromethane mixture contrasts with the nine-line pattern observed when water is used as the solvent. This effect arises from the fact that the hyperfine constant of one nitrogen is not exactly half that of the other, as shown in Table 1. This difference is accentuated when NaOH is added to the aqueous solution (Fig. 2). The hyperfine structure could not be resolved in any of the experiments. The linewidth of 0.69 G

indicates that a very small amount of spin density is located on the pyrazolyl ring

In concentrated solutions of **PzNN** in a toluene/dichloromethane (3:1) mixture, additional resonances

Table 1
Coupling constants of **PzNN** and **PzIN** radicals (in G) obtained by simulation of spectra with SIMFONIA Bruker EPR program

	Solvent	a_N	a_{Me}	$a_{H_{pyr}}$	$a_{N_{pyr}}$
PzNN	H ₂ O	8.33	0.185	0.315	0.094
	H ₂ O/-OH	8.45	0.205	0.279	0.064
PzIN	H ₂ O	9.94/4.43			
	H ₂ O/-OH	10.34/4.20			

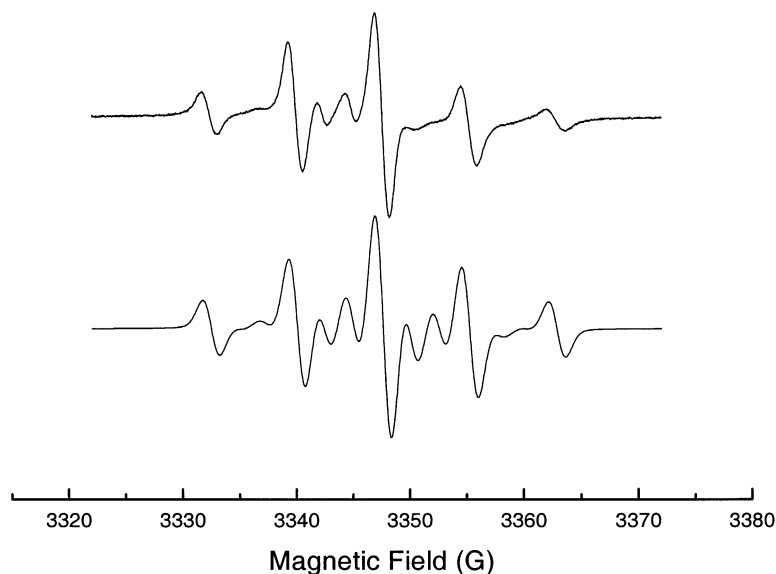


Fig. 3. EPR spectrum of a dilute dichloromethane/toluene (1:3) solution of **PzNN** (top — experimental, bottom — simulated (with $a_{\text{N mono}} = 7.66$ G, $\Delta B = 1.4$ G, with $a_{\text{N tri}} = 2.53$ G, $\Delta B = 1.6$ G at a 1:1 ratio).

are observed in the EPR spectrum upon lowering the temperature (Fig. 3), meaning that another paramagnetic species is present in solution. These lines are absent in very dilute solutions or in solutions in more polar solvents. The spectrum could be fairly well reproduced in the low field region by adding to the simulated spectrum of the monoradical a component corresponding to trimeric aggregates with a coupling a_{N} one third of the monomer value (simulated with $a_{\text{N mono}} = 7.66$ G, $\Delta B = 1.4$ G, with $a_{\text{N tri}} = 2.53$ G, $\Delta B = 1.6$ G at a 1:1 ratio, Fig. 3). Simulation with dimeric or tetrameric and higher aggregates did not reproduce the spectrum. These intermediate lines grow in intensity as the temperature is lowered and as the concentration is raised, showing the displacement of the equilibrium with temperature decrease and concentration increase towards formation of the trimers. The appearance of such lines indicates that the three unpaired radicals are spread over the three molecules and interact with an exchange coupling constant $J \gg a_{\text{N}}$.

Some information about the type of aggregates can be extracted from these data. Should linear trimeric aggregates be present, two types of signals would be expected, since it is expected that between two hydrogen bonds at a long distance, the radicals at the extremes would not interact with each other. Hence, the resulting spectrum would be the spectrum of the central radical in exchange with the two others (triradical spectrum), added to the spectra of the two radicals at the extremes in exchange with the central one (biradical spectrum). As this kind of pattern was not observed, we could conclude that the aggregates are cyclic ones. The presence of aggregates was further confirmed by the X-band EPR spectra in frozen solution. The $\Delta M_{\text{S}} = \pm$

1 signal shows a fine structure pattern arising from dipolar interactions between the three electrons, although it could not be resolved using the X-band spectrometer, as the zero-field splitting parameters of the aggregate are small because of the large effective distance between the radical centres. Importantly, a $\Delta M_{\text{S}} = \pm 2$ half-field signal characteristic of species of spin $S \geq 1$ was detected (Fig. 4).

In the case of **PzIN**, no additional lines were observed at low temperatures in the toluene/dichloromethane solution EPR spectra, but the broadening of the seven lines could hide the intermediate lines due to the presence of a small fraction of three imino nitroxides in exchange. The detection of the

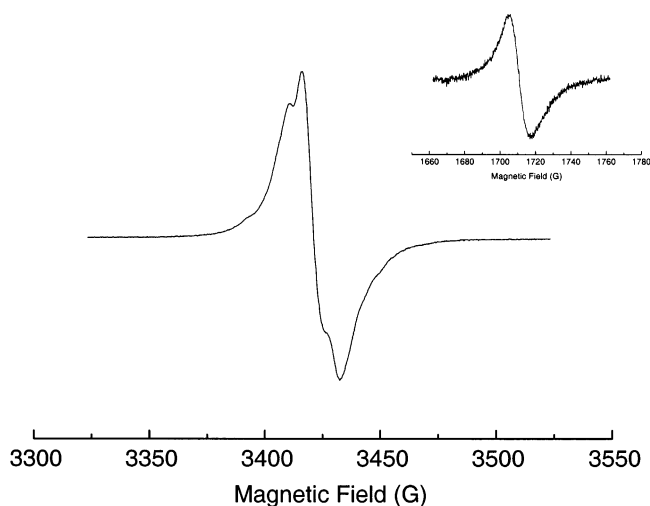


Fig. 4. EPR spectrum of a frozen solution in dichloromethane/toluene (1:3) of **PzNN** at 9 K (a: $\Delta M_{\text{S}} = \pm 1$ line; b: $\Delta M_{\text{S}} = \pm 2$ line).

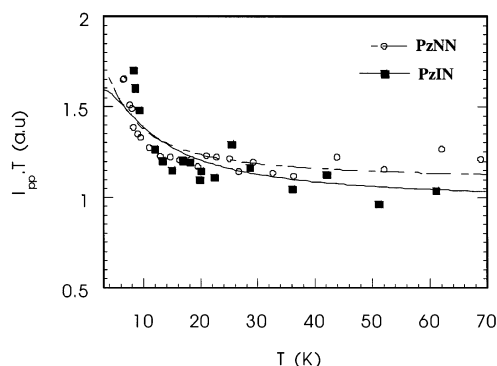


Fig. 5. Evolution of the product of the intensity of the half-field signal and the temperature plotted against the temperature for **PzNN** and **PzIN**.

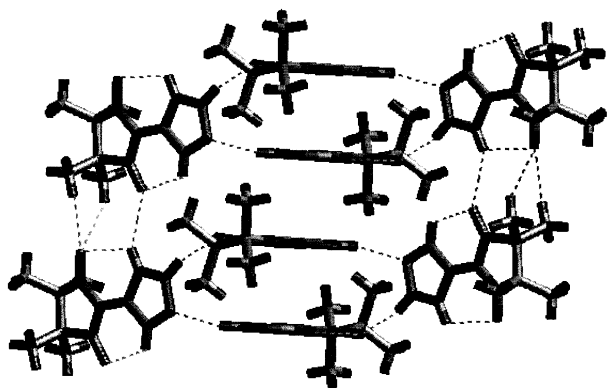


Fig. 6. A view of the crystal structure of **PzNN**.

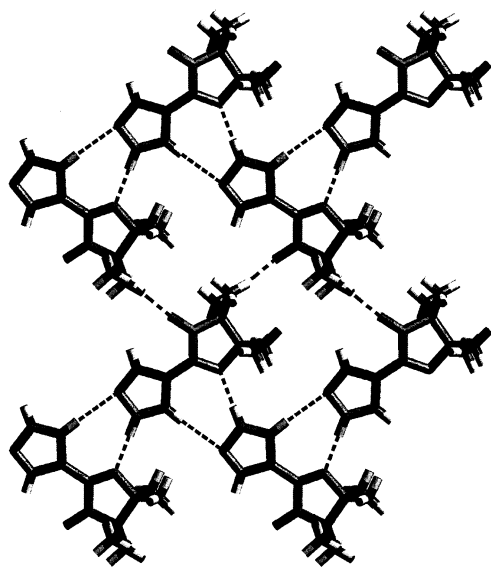


Fig. 7. A view of the crystal structure of **PzIN** along the *ac* plane.

half-field signal in frozen solution unambiguously proved that this compound also forms some type of aggregate(s), although the lack of a hyperfine structure negates the assignment of its (their) nature.

It was of great interest to determine the nature of the magnetic interactions that act via the hydrogen bonds in these aggregates. Thus, the intensity of the half-field signals was followed in the 6–80 K temperature range. As the $IT = f(T)$ curve rises when temperature is lowered (Fig. 5), the presence of a ferromagnetic interaction within the aggregates was confirmed. The gap assuming a quartet ground state was estimated to be $J/k = +2$ K for both compounds using an equilateral triangular model to fit the data.

The non-covalent cyclic linkage within the aggregates that are formed could either be through $[\text{NH} \cdots \text{N}]$ hydrogen bonds, as in the case of other pyrazole derivatives, [7,20] or through $[\text{NH} \cdots \text{O}]$ hydrogen bonds from the pyrazolyl moiety to the NO groups of the nitronyl nitroxide unit. In order to clarify this point we turned to X-ray crystallography.

The X-ray crystal structure of **PzNN** (Fig. 6), which pertains to the $P\bar{1}$ space group, has a unit cell comprised of two inequivalent molecules, which present a dihedral angle between the imidazolyl and the pyrazolyl rings of 1 and 9°, respectively. These values are peculiarly low compared with similar compounds of this family, and can be justified by the presence of weak intramolecular hydrogen bonds between the CH of the pyrazolyl ring and the NO groups of the α -nitronyl nitroxide ring. In principle, this conformation should lead to optimum delocalisation of the spin density from the radical unit to the pyrazolyl ring, and thus to the NH group. The secondary structure in the solid can be described as cyclic tetramers united by both $[\text{NH} \cdots \text{N}]$ and $[\text{NH} \cdots \text{ON}]$ bonds. These tetramers are piled up along the *a* axis by π – π stacking interactions between the pyrazolyl rings of the central molecules and weak $[\text{CH} \cdots \text{ON}]$ hydrogen bonds between both the methyl groups attached to the imidazolyl ring and the CH groups of the pyrazolyl ring and NO groups of neighbouring molecules located at the “sides” of the tetramer (Fig. 6).

PzIN crystallises in the orthorhombic $Pna2_1$ space group. The dihedral angle between the imidazolyl and the pyrazolyl rings is 11°. The molecules are linked by hydrogen bonds between the NH group of the pyrazolyl ring and the nitrogen atom of the imino group, leading to the formation of chains along the *c* direction (Fig. 7). In turn, these chains are bound together in the *b* direction by hydrogen bonds between the methyl and the NO groups of the radical units.

The temperature dependence of the paramagnetic susceptibility χ of the crystalline samples of both compounds was measured with a SQUID susceptometer in the temperature range from 2 to 300 K. The room temperature value of $\chi_m T$ (about 0.375 emu K mol^{−1}) is as required for isolated $S = 1/2$ paramagnetic centres with no magnetic interactions, in agreement with the Curie constant. The plot of the product of paramag-

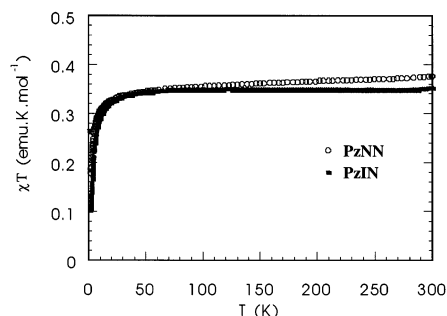


Fig. 8. χT versus T plot as determined by SQUID measurement for **PzNN** and **PzIN**.

netic susceptibility and temperature versus temperature (Fig. 8) reveals a decrease in the former when lowering the temperature below 10 K, meaning that antiferromagnetic interactions are dominant at these temperatures. The curves could be fitted to a Curie–Weiss law, with $\theta = -3.1$ and -2.1 K for **PzIN** and **PzNN**, respectively.

3. Conclusions

Two new nitroxide radical ligands based on the pyrazole ring have been synthesised and characterised. Using EPR spectroscopy it has been shown that supramolecular trimeric aggregates form in solution when lowering the temperature. These isolated supramolecular objects are of great interest in understanding the role of the hydrogen bond as a pathway for magnetic exchange. Theoretical computations and NMR experiments are underway to determine the type of aggregates formed. Crystalline structures have been resolved for both compounds, revealing other kinds of patterns formed by hydrogen bonds in the solid state. The competition between the oxygen and nitrogen hydrogen bond acceptors in the crystal structures, which appears in the case of these radicals to be very finely balanced, is notable. Other derivatives of pyrazole bearing hydrogen bond acceptors maintain the trimeric pyrazole supramolecular synthon [4]. These types of packing generate weakly antiferromagnetic interactions. The next step in our research is to use these ligands for the preparation of transition metal complexes, work towards which is in progress in our laboratory.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 155086 for **PzNN**, 155087 for **PzIN**. Copies of this information may be obtained from

The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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