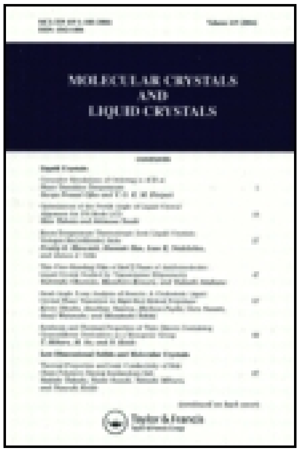

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HYDROGEN-BONDED ACID-BASE MOLECULAR COMPLEXES OF NITRONYLNITROXIDES

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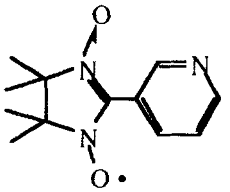
Abstract Intermolecular hydrogen-bonded complexes of *p*-nitronylnitroxide benzoic acid (*p*-NNBA-H) with *m*- and *p*-pyridylnitronylnitroxides (*m*- and *p*-PYNN, respectively) were prepared. The *m*-PYNN•*p*-NNBA-H complex crystallizes into the monoclinic $P2_1/c$ space group [a=6.685(3) Å, b=17.657(2) Å, c =22.169(1) Å, β =92.90(1)°,V=2613(1) Å^3, Z=4], while the crystal of *p*-PYNN•*p*-NNBA-H belongs to the monoclinic $P2_1/n$ space group[a=12.199(3) Å, b=23.265(4) Å, c=9.522(2) Å, β=101.84(2)°,V=2644.9(9) Å^3, Z=4]. In their crystals, there is an intermolecular hydrogen bond between the nitrogen atom on the pyridyl ring of PYNN and one of the oxygen atoms of the carboxyl group of *p*-NNBA-H. The intermolecular N•••O distances are 2.642(5) Å in *m*-PYNN•*p*-NNBA-H and 2.613(6) Å in *p*-PYNN•*p*-NNBA-H, indicating rather intense hydrogen bonds. The magnetic properties of *m*-PYNN•*p*-NNBA-H and *p*-PYNN•*p*-NNBA-H are well interpreted in terms of the singlet-triplet model with $2J_{AF}/k_B$=-16.0 K and the Curie-Weiss law with θ=-0.68 K, respectively.

INTRODUCTION

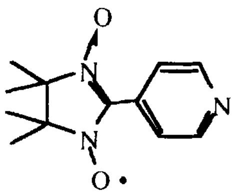
Nitronylnitroxides have been extensively studied as a spin source of molecule-based magnetic materials, because of their potentiality giving ferromagnetic intermolecular couplings.[1] We have undertaken a systematic study of the *m*- and *p*-pyridyl nitronylnitroxide radicals[2] (abbreviated as *m*- and *p*-PYNN, respectively), making characteristic chemical modifications such as *N*-alkylation,[3] *N*-oxidation[4] and *N*-protonation.[5] In the course of the studies, it is found that the PYNNs act as a base molecule and form complexes with various organic acids, such as squaric acid, fumaric acid, hydroquinone. Such an acid-base interaction, which is characteristic of molecule-based materials, would expand the variety of the crystal structures and magnetic properties of molecule-based magnetic materials.

In this work, we prepared acid-base molecular complexes between *m*- or *p*-PYNN and a nitronylnitroxide acid, *p*-nitronylnitroxide benzoic acid (abbreviated as *p*-

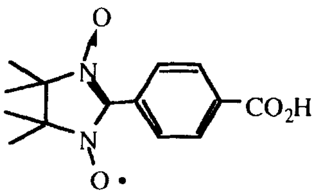
NNBA-H). We describe the crystal structures and magnetic properties of the two heterogeneous complexes, *m*-PYNN•*p*-NNBA-H (**1**) and *p*-PYNN•*p*-NNBA-H (**2**).



m-PYNN



p-PYNN



p-NNBA-H

EXPERIMENTAL

The parent radicals, *m*- and *p*-PYNN and *p*-NNBA-H, were prepared according to the literature method.[2,6,7] The single crystals of the complexes **1** and **2** were obtained by slow evaporation of the ether solutions which contained stoichiometric amounts of the corresponding parent radicals.

X-ray diffraction data were collected on RIGAKU AFC-5 automatic four-circle diffractometer with graphite-monochromatized Mo K_α radiation (λ=0.71073 Å). Unit cell dimensions were obtained by a least-squares refinement using 25 reflections with $20° < 2\theta < 25°$. During data collection, the intensities of three representative reflections were measured as a check on crystal stability, and no loss was shown. Structures were solved by direct methods (SHELX-86[8]) and refined by block-diagonal least-squares technique (UNICS III[9]). All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were found by differential Fourier methods, and were not refined. Details of the crystallographic parameters are summarized in Table I.

The dc magnetic susceptibilities were measured in the temperature range of 3-280 K in the field of 1 T on a Faraday balance. The paramagnetic susceptibility, χ_p, was calculated by subtracting the diamagnetic susceptibilities which were obtained, assuming that the paramagnetic component follows the Curie law at high temperatures.

CRYSTAL STRUCTURES

The crystal of **1** belongs to the monoclinic $P2_1/c$ space group, where one *m*-PYNN•*p*-NNBA-H unit is crystallographically independent. Figure 1 shows the asymmetric unit. The *m*-PYNN and *p*-NNBA-H molecules are connected by an intermolecular hydrogen

Table I. Crystallographic data and experimental parameters for **1** and **2**.

	1	2
crystal system	*monoclinic*	*monoclinic*
a/Å	6.685(3)	12.199(3)
b/Å	17.657(2)	23.265(4)
c/Å	22.169(1)	9.522(2)
β/deg.	92.90(1)	101.84(2)
V/Å^3	2613(1)	2644.9(9)
D(calc), g/cm^3	1.300	1.285
space group	$P2_1/c$	$P2_1/n$
Z	4	4
μ/cm^{-1}	1.013	1.001
radiation	Mo $K\alpha$ (λ = 0.71073 Å) graphite monochromator	
2θ range, deg	4.0-55.0	4.0-55.0
no. collected	6868	6656
no. obsd ($\lvert F_0\rvert > 3.0\sigma(F_0)$)	2676	3439
R	0.0839	0.0830
R_w	0.0810	0.0843

bond between the nitrogen atom N(5) on the pyridine ring and the oxygen atom O(20) of the carboxyl group, as depicted as the broken line in Figure 1. The intermolecular, interatomic distance N(5)•••O(20) is 2.642(5) Å, indicating a rather intense hydrogen bond. The dihedral angle between the pyridyl and phenyl rings in the pair is calculated to be 6.4(1)°. The C-O distances in the carboxyl group of *p*-NNBA-H are not equivalent; 1.311(6) Å of C(37)-O(20) and 1.203(6) Å of C(37)-O(21). The proton in the hydrogen bond is thought to attach to the carbonyl group.

Figure 2 shows a projection of the crystal structure along the *a* axis. The acid-base pairs form a head-to-tail dimer (namely, radical tetramer) with an inversion symmetry. In the radical tetramer, there are shorter distances between the NO groups of *m*-PYNN and *p*-NNBA-H. The intermolecular distances from O(2) of *m*-PYNN to O(19) and N(23) of *p*-NNBA-H are 3.265(5) and 3.381(5) Å, respectively. The shortest distance between the pyridyl and phenyl rings is 3.482(6) Å of C(16)•••C(35). In addition, the tetramer units pack like linoleum, and form a two-dimensional layer parallel to the *bc* plane, although there is no significant overlap between the π orbitals of the organic radicals in the intertetramer arrangement. Along the *a* axis, there is a screw of the layer, forming the bulk crystal.

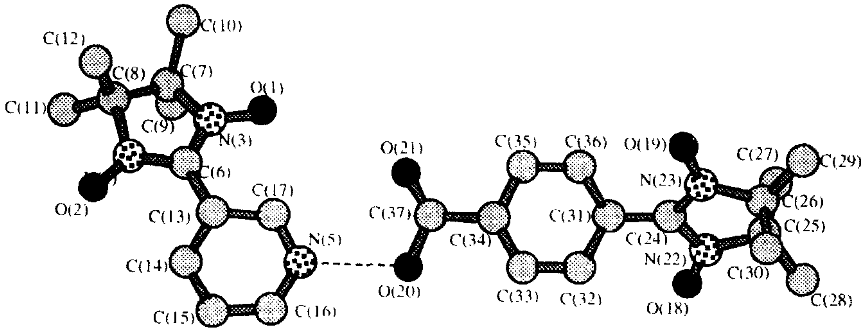


FIGURE 1 Asymmetric unit of **1**.

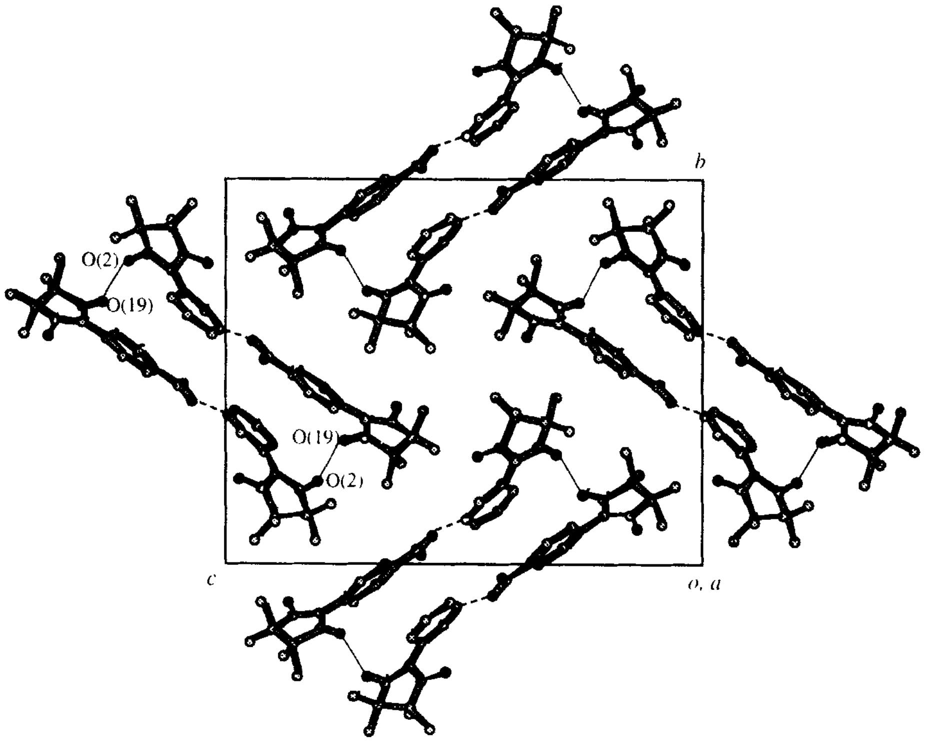


FIGURE 2 A projection of the structure of **1** along the *a* axis.

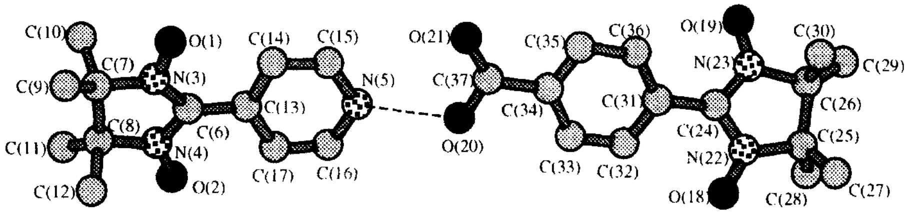


FIGURE 3 Asymmetric unit of **2**.

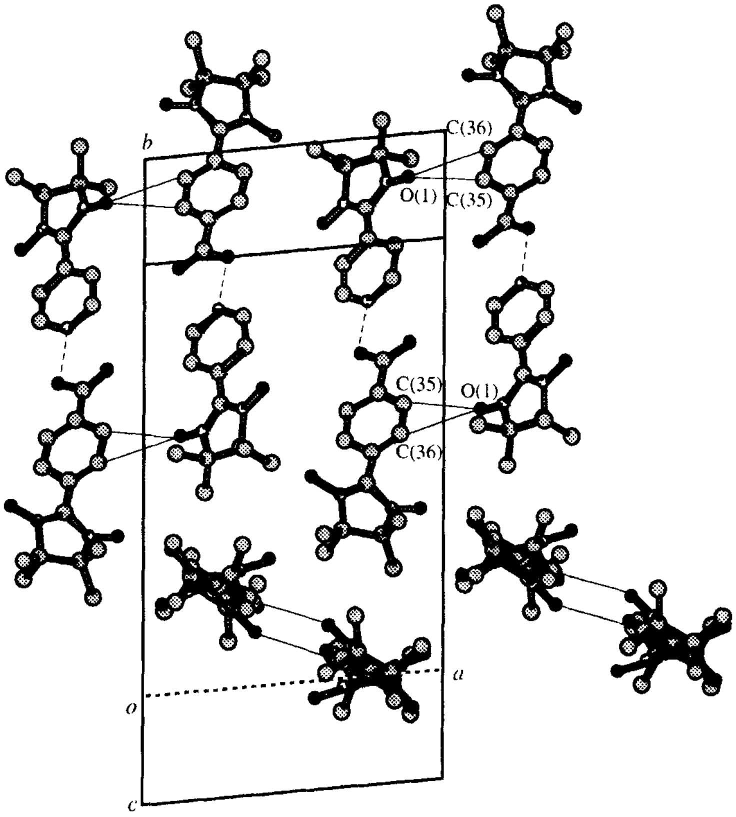


FIGURE 4 A view of the structure of **2**.

The complex **2** crystallizes into the monoclinic $P2_1/n$ space group, where one *p*-PYNN•*p*-NNBA-H unit is crystallographically independent. Figure 3 shows the asymmetric unit. In the pair, *p*-PYNN and *p*-NNBA-H are connected by an intermolecular hydrogen bond between the nitrogen atom N(5) of the pyridyl ring and the oxygen atom O(20) of the carboxyl group with an intermolecular, interatomic distance of 2.613(6) Å. The carboxyl group is asymmetric: the distances of C(37)-O(20) and C(37)-O(21) are 1.337(6) and 1.224(7) Å, respectively. The dihedral angle between the pyridyl and phenyl rings in the pair is 7.8(1)°. Figure 4 shows a view of the structure. In the unit cell, the hydrogen-bonded pairs are arranged head-to-tail with an inversion symmetry, forming a tetramer unit. In the unit, there is no short contact between the NO groups, as observed in the crystal of **1**, but the NO groups of *p*-PYNN is rather close to the phenyl ring of *p*-NNBA-H. The shorter intermolecular, interatomic distances are 3.291(6) Å of O(1)•••C(35) and 3.368(5) Å of O(1)•••C(36).

We have succeeded in making acid-base pair complexes, **1** and **2**. In their crystals, *m*- or *p*-PYNN and *p*-NNBA-H are connected by the intermolecular hydrogen bond. The distances of the hydrogen bonds; 2.642 Å in **1** and 2.613 Å in **2**, are shorter by about 0.4 Å than the sum of the van der Waals radii of oxygen and nitrogen, suggesting rather strong interactions. From the asymmetric shape of the carboxyl group, the proton in the intermolecular hydrogen bond is thought to be located at the carboxyl group in either **1** or **2**. This is further supported by absence of the stretching bands of the carboxylate in their IR spectra (not shown).

MAGNETIC PROPERTIES

The open circles in Figure 5 show the temperature dependence of the paramagnetic susceptibilities χ_p of **1**. In this figure, PYNN•*p*-NNBA-H (FW=511.58) is taken as a molar unit and the horizontal axis is in a logarithmic scale. The value of χ_p of **1** increases with decreasing temperature down to 10 K and, after passing a maximum, it turns to decrease, approaching to zero at the absolute zero. The behavior is found to be explained with the Bleany-Bowers expression[10] for antiferromagentic dimers. The solid curve going through the plots for **1** is the theoretical best fit with g=2 (fixed) and the intradimer antiferromagnetic coupling of $2J_{AF}/k_B$=-16.0 K. The closed circles in Figure 5, on the other hand, show the temperature dependence of χ_p of **2**. They show a monotonous increase down to 3 K. The solid curve fitted to the plots for **2** is the best fit of the Curie-Weiss law with g=2 (fixed) and θ=-0.68 K.

The magnetic properties of **1** are well interpreted in terms of the antiferromagentic dimer. There are two possible intermolecular contacts which are responsible for the observed magnetic interaction: one is the intermolecular hydrogen bond and the other is the direct interaction between the NO groups. The former possibilities is excluded, because the results of **2**, which also involves similar intermolecular hydrogen bonds, show the weak magnetic interaction.

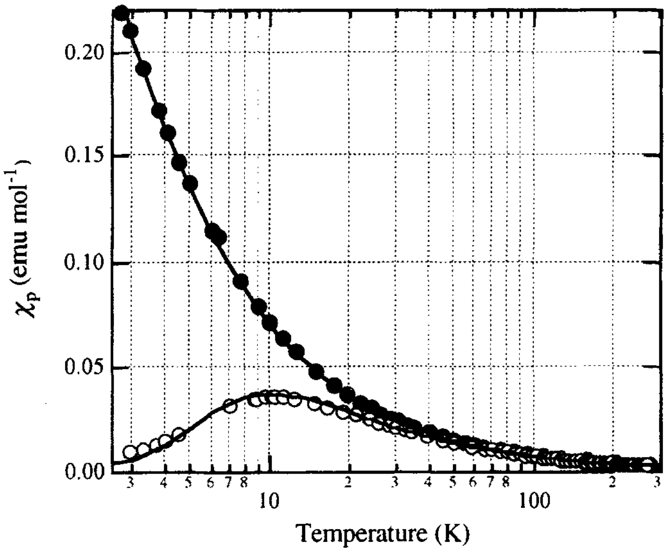


FIGURE 5 Temperature dependence of the paramagnetic susceptibilities of **1** (open circle) and **2** (closed circle). The solid curves are theoretical ones (see the text).

CONCLUSION

The intermolecular hydrogen-bonded complexes, *m*-PYNN•*p*-NNBA-H and *p*-PYNN•*p*-NNBA-H were prepared. Although there is a precedent for heterogeneous molecular complex of organic radicals,[11] they are the first organic radical complex which is formed by the acid-base interaction. In their crystals, the acid and base radicals are connected by the strong hydrogen bond between the pyridyl ring and the carboxyl group. Unfortunately there is little magnetic interaction through the hydrogen bond, but the methodology of hetero-radical connections could be useful to expand the variety of molecule-based magnetic materials, for instance, toward achievement of organic ferrimagnets by co-crystallization of hetero-radicals with different spin multiplicity.

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