

2-Cyano-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide as key compound for preparation of nitronyl and imino nitroxides

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Abstract. A series of nitronyl and imino nitroxides: amides **2**, **13** (NN-C(O)-NH₂, IN-C(O)-NH₂), iminoethers **3a,b**, **15** (NN-C(NH)-OR (R = CH₃, 2-Pr), IN-C(NH)-OCH₃), carboxylates **4**, **14a-c** (NN-C(O)-OK, IN-C(O)-OX (X = K⁺, (*n*-Bu)₄N⁺)), and paramagnetic tetrazoles **5**, **7-12** were synthesized from 2-cyano-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide (NN-C≡N). The crystal and molecular structure was determined for all compounds except **4**, **14c**, and **15**.

Key words. Nitronyl nitroxide – imino nitroxide – structure – magnetic properties – molecular materials.

1. INTRODUCTION

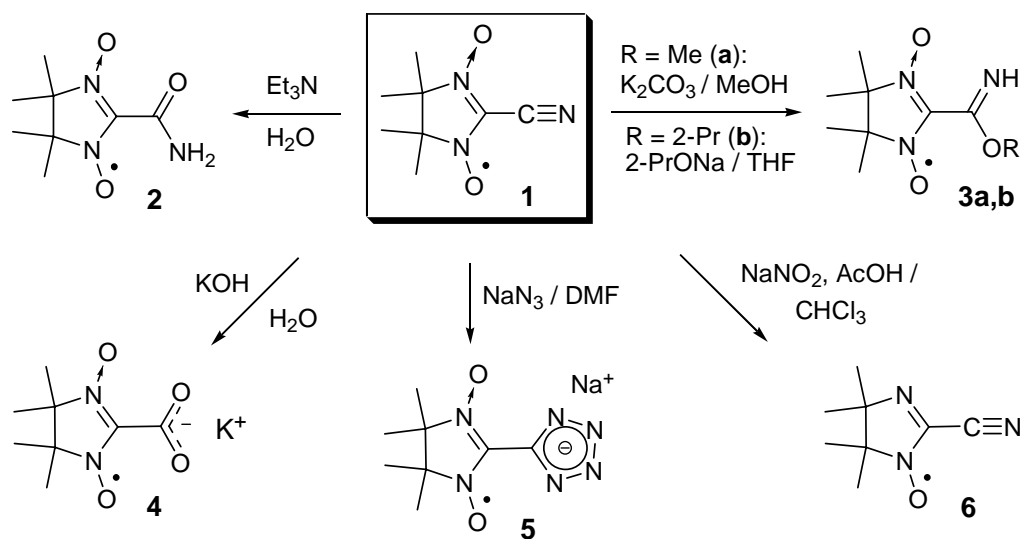
Molecular magnets have recently received considerable attention, and reliable strategies for designing such materials have been elaborated [1,2,3]. Molecular magnets based on metal-nitroxide complexes are very attractive as compounds that are highly stable under ambient conditions and may be selectively functionalized for variation of physical parameters. Therefore, active studies are under way in the field of chemical design of polyfunctional nitroxides, whose coordination to paramagnetic metal ions will lead to highly dimensional heterospin systems with specified structures and energies of exchange interactions between the odd electrons of the paramagnetic centers.

In this communication we report on the synthesis and structural investigation of a series of nitronyl and imino nitroxides derived from 2-cyano-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide (**1**).

2. RESULTS AND DISCUSSION

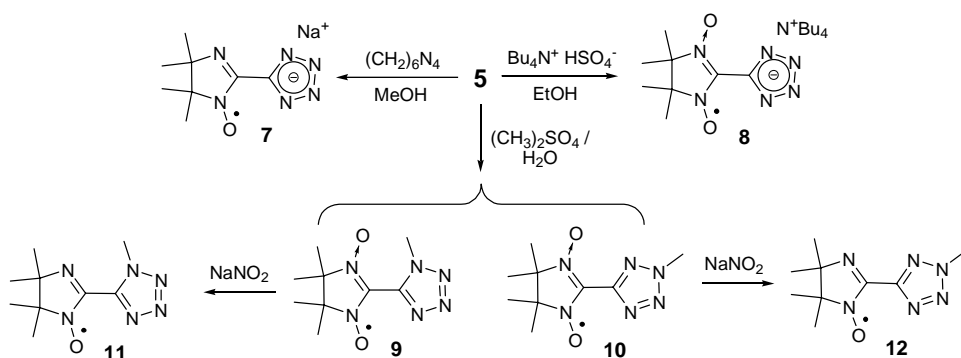
The increasingly wide use of multifunctional nitronyl and imino nitroxides has stimulated the development of new synthetic approaches. One of these is modification of the substituent in the structure of nitroxide, leaving the free valence unaffected. We have concentrated on nitrile **1** [1], in which increased electrophilicity of the –C≡N group caused by the high electron-accepting effect of the nitronyl nitroxide fragment could hopefully lead to easy addition of nucleophilic reagents at the C≡N bond, giving new chelate-forming nitronyl nitroxides. Indeed, as shown in Scheme 1, nitrile **1** reacts readily with various nucleophiles at room temperature or with gentle heating. Thus, spin-labeled amide **2** was prepared by stirring a suspension of nitrile **1** in water in the presence of Et₃N (yield 50%) [5]. Stirring a methanol solution of **1** in the presence of Na₂CO₃ readily gave imino ether **3a** [4]. The same procedure could not be applied to synthesis of homolog **3b**, because **1** is insoluble in isopropanol. Iminoether **3b** was prepared by reaction of **1** with sodium isopropanoxide in THF in a yield of 50%. Potassium nitronyl nitroxide carboxylate **4** was synthesized by hydrolysis of paramagnetic nitrile **1** in the presence of an equimolar amount of KOH. The reaction product, salt **4**, is a dark violet powder insoluble in benzene, ether, and acetone, but readily soluble in water, MeOH, EtOH, and DMF. In solution, salt **4** is unstable and gradually decarboxylated into NN-H. The azide ion easily added at the C≡N bond of **1** in DMF in the presence of NH₄Cl, forming a paramagnetic derivative of tetrazole **5** [6].

On the other hand, mild reducing agents can selectively modify the nitronyl nitroxide fragment of **1**. Thus, imino nitroxide **6** was synthesized in a high yield (~75%) by reduction of **1** with NaNO_2 .



Scheme 1

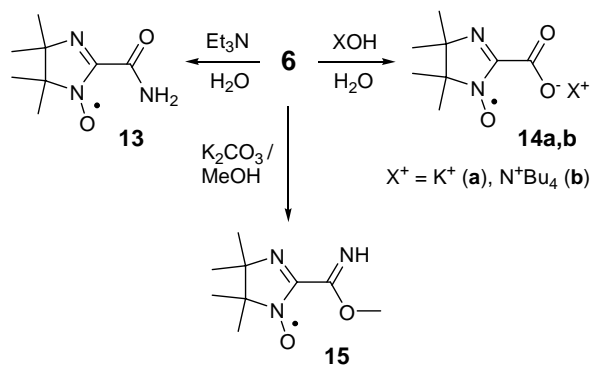
Having solved the problem of synthesis of nitroxides **2-6**, one can plan syntheses of new paramagnetic ligands from these compounds. Scheme 2 demonstrates some selective transformations using spin-labeled tetrazole **5** as the starting compound. We have succeeded in synthesizing imino nitroxide **7** by reduction of **5** with $(\text{CH}_2)_6\text{N}_4$ [1]. Ion exchange reaction was used to synthesize a spin-labeled tetrazole salt soluble in both polar and low polar solvents. Alkylation of **5** gave a mixture of isomers **9** and **10**. From these isomers we synthesized 2-(methyltetrazolyl)imidazoline imino nitroxides **11** and **12**.



Scheme 2

Nitrile **6** possesses slightly lower reactivity in nucleophilic additions at the $\text{C}\equiv\text{N}$ bond (Scheme 3). Thus, **6** is unreactive with NaN_3 and does not form **7** below its decomposition point. Nevertheless, the reactivity of **6** proved to be sufficient for syntheses of paramagnetic ligands of interest from the viewpoint of coordination chemistry. Mild hydrolysis of **6** led to the formation of amide **13**. Hydrolysis in more rigid conditions in the presence of an equimolar amount of an appropriate base XOH ($\text{X} = \text{K}^+$, $(n\text{-Bu})_4\text{N}^+$) gave imino nitroxide carboxylates **14a,b**. Imino nitroxide carboxylate **14a** is a crystalline substance shaped as thin brick red plates insoluble in benzene, ether, acetone, and 2-propanol, sparingly soluble in EtOH and DMF, and readily soluble in water and MeOH. Carboxylic

salt **14b** readily dissolves in low polar solvents. TLC monitoring of solutions of salts **14a,b** stored for a few days at room temperature did not reveal any decomposition or decarboxylation products, as was the case with **4**. Stirring a methanol solution of **6** in the presence of Na_2CO_3 for a few hours led to imino ether **15** (red oil at room temperature).



Scheme 3

Sample purity of nitroxides **2-15** was confirmed by elemental analysis and by the fact that their effective magnetic moment at room temperature is close to the theoretical value (1.73 B.M.).

Molecular and crystal structures of all *crystalline* radicals except **4** were completely solved by X-ray structure analysis (examples follow).

1. Solid compounds **2** and **13** have a polymer chain structure with bifurcated intermolecular hydrogen bonds. As an example Fig. 1 shows the molecular and crystal structure of **2**. (CCDC Nos. 217543 (**2**), 217536 (**13**)).

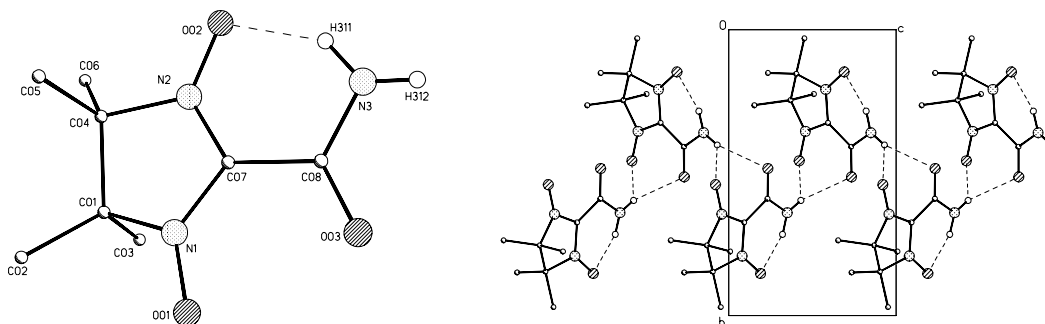


Figure 1. Molecule **2** and projection of the structure onto (100).

2. Iminoethers **3a,b** are similar in molecular and crystal lattice structure. As in **2**, the structure has intramolecular H-bonds, whereas intermolecular H-bonds are absent.

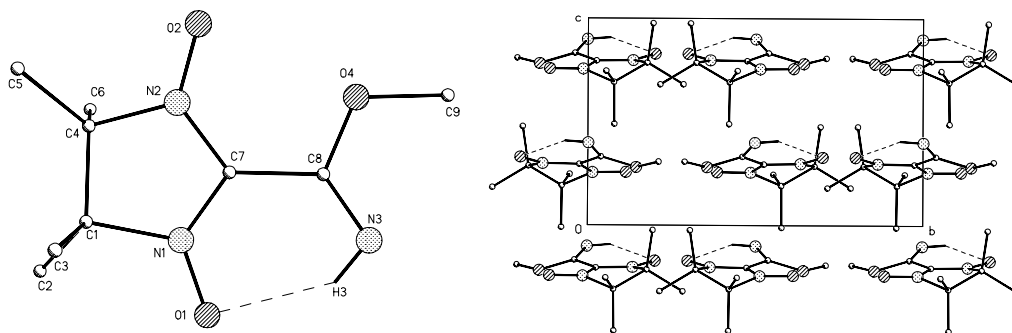


Figure 2. Molecule 3a and projection of the structure onto (100).

3. An X-ray diffraction study of **6** indicated that the crystal structure of **6** is identical to that of **1** [8]. The molecule also has $2mm$ symmetry (CCDC No. 217584).

4. In carboxylate **14a**, the imino nitroxide and carboxyl fragments are coplanar. Solid **14a** has a layered structure.

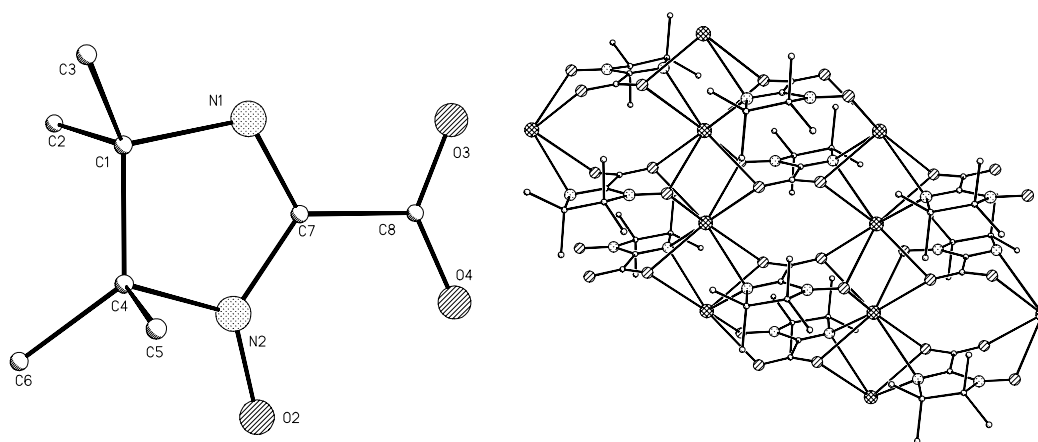


Figure 3. K-salt 14a and fragment of layer in solid 14a. Main distances (Å): K-O 2.68(1)-2.93(1), K-N 2.92(1)-2.99(1); C-O 1.23(1); K-K' 3.49(1).

5. Previously, we have published X-ray structure analysis data for paramagnetic derivatives of tetrazole **5**, **9**, **10** [6]; **7** [7]. The structure of the anion in **8** is identical to that in **5**.

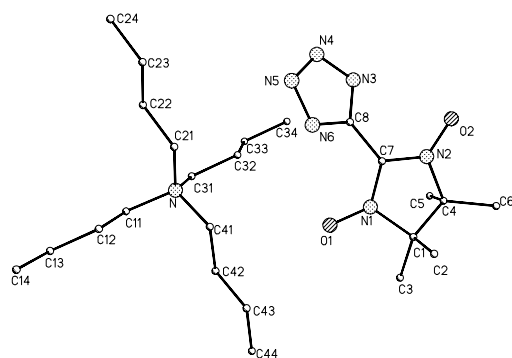


Figure 4. Molecular structure of **8**.

Solid molecules **11** and **12** differ in the value of the angle between the planes of the O-N-C=N fragment of the imidazoline cycle and tetrazole ring: 36.8 and 37.3° in **11** versus 20.8 and 30.0° in **12** in two crystallographically independent molecules. As an example Fig. 5 shows the molecular and crystal structure of **12**.

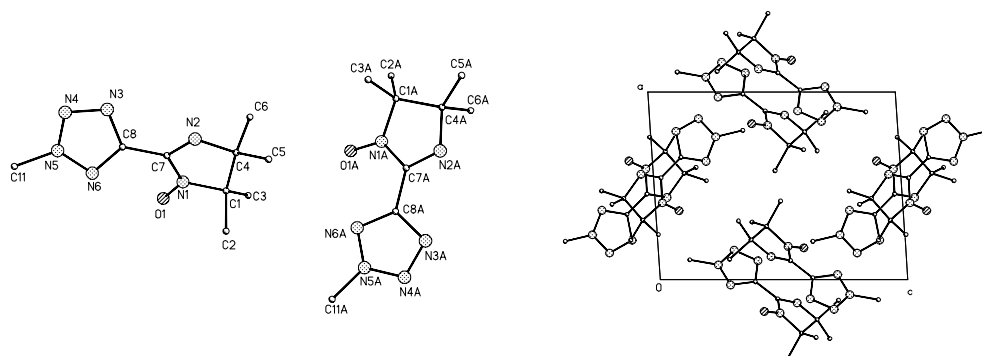


Figure 5. Molecular structure of **12**.

Further investigations are under way to make it possible use these radicals as ligands of magnetically active transition metals.

Acknowledgments

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