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Nitronyl nitroxides containing tetrazole substituents and metal complexes with spin-labeled tetrazole

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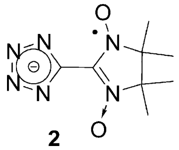
Abstract

The first nitronyl nitroxides containing tetrazole substituents: sodium salt of 2-(1*H*-tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl (Na(**2**)), 2-(1-methyl-1*H*-tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl (**3**), and 2-(2-methyl-2*H*-tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl (**4**) have been synthesized. The structures of **2**–**4** were confirmed by X-ray analysis. For **2**, a tendency to form highly dimensional structures by interaction with transition metals has been found. Mn^{II} tends to form diamond-like packing with **2** using $[Mn(H_2O)_6]^{2+}$ and $[Mn(\mathbf{2})_3]^-$ building blocks. Ni^{II} forms layered structures from the binuclear cations with the aid of the bridging nitroxide $[En_2Ni(\mathbf{2})NiEn_2]^{3+}$ and H-bonded ClO_4^- groups.

Keywords: Nitronyl nitroxide; Tetrazole; Manganese complexes; Nickel complexes

1. Introduction

Formation of layered or framework structures in solid molecular magnets is an essential condition for a magnetic phase transition to the magnetically ordered state [1]. One of the factors that favor the formation of highly dimensional structures is using polyfunctional ligands that are symmetric with respect to the donor groups. In the field of molecular ferromagnet design based on transition metal complexes with nitroxides, this approach was realized in Refs. [2–5]. This paper reports on the procedure for the synthesis of tetrazole-substituted nitronyl nitroxide **2** and examines the possibility of preparation of highly dimensional heterospin structures based on metal complexes with **2**. In the series of symmetric paramagnetic azole derivatives, compound **2** has a quite harmonic structure because the anion molecule may have C_{2v} symmetry and perform the bridging function in honeycomb- and diamond-like structures.



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2. Experimental

2.1. Materials and instruments

The synthesis of 2-cyano-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide from the corresponding 2-bromoderivative was described previously [6,7]. Other reagents were commercially available and used

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without further purification. IR spectra were recorded for KBr pellets on a Vector 22 (Bruker) spectrometer.

2.2. Syntheses of compounds

2.2.1. Sodium salt of 2-(1*H*-tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl dihydrate (Na(**2**))

A mixture of 2-cyano-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl (**1**) (300 mg, 1.6 mmol), NaN_3 (110 mg, 1.7 mmol), and NH_4Cl (10 mg, 0.19 mmol) in DMF (6 ml) was stirred for 2 h at 60 °C. The solvent was removed in vacuum. The residue was washed with ether and ethyl acetate, and then dissolved in hot ethanol (25 ml). The solution was filtered and concentrated to ~1 ml and then diluted with ether (10 ml). The blue powder of Na(**2**) was filtered-off on a frit. Yield: 350 mg (77%). Noteworthy, the crude product showed an IR spectrum identical to that of the analytical sample and could be used in reaction without further purification. The analytical sample was prepared by slow evaporation of a methanol–isopropanol solution, which gave rise to blue needles suitable for an X-ray analysis. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 830, 869, 1075, 1143, 1169, 1218, 1307, 1348, 1377, 1412, 1456, 1576, 1625, 2992, 3210 br, 3473 br. Anal. Found: C, 33.9; H, 5.7; N, 29.7. Calc. for $C_8H_{12}N_6NaO_2 \cdot 2H_2O$: C, 33.9; H, 5.7; N, 29.7%. m.p. (the color of crystals changes to orange and melting occurs): 218–220 °C.

2.2.2. 2-(1-Methyl-1*H*-tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl (**3**) and 2-(2-methyl-2*H*-tetrazol-5-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyl (**4**)

To a solution of Na(**2**) (250 mg, 0.88 mmol) and KOH (1.0 g) in water (1.5 ml) was added $(CH_3)_2SO_4$ (150 mg, 1.2 mmol). The reaction mixture was stirred at room temperature for 20 min and extracted with $CHCl_3$ (6 × 10 ml). The extracts were dried with Na_2SO_4, filtered, and concentrated to ~3 ml. The resulting solution was chromatographed on a silica gel column (1.5 cm × 14 cm) using ethyl acetate as eluent. After evaporation of the eluate, the greenish blue powder was dissolved in CH_2Cl_2 (2 ml), then heptane (2 ml) was carefully added, and the mixture was kept in an open flask at 25 °C. Crystals of two different types were obtained; they were separated manually and used for an X-ray investigation. **3**: large greenish blue crystals. Yield: 140 mg (66%). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 694, 730, 758, 822, 867, 1108, 1135, 1150, 1168, 1188, 1212, 1265, 1372, 1398, 1469, 2944, 2991. Anal. Found: C, 45.0; H, 6.3; N, 35.2. Calc. for $C_9H_{15}N_6O_2$: C, 45.2; H, 6.3; N, 35.1%. m.p.: 196–197 °C. **4**: greenish blue needles. Yield: 31 mg (15%). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 698, 760, 827, 864, 1022, 1070, 1138, 1168, 1199, 1220, 1308, 1362, 1430, 1460, 2940, 2986. m.p.: 151–152 °C.

2.2.3. $[En_2Ni(\mathbf{2})NiEn_2](ClO_4)_3$ (**5**)

A solution of $Ni(CH_3COO)_2(H_2O)_4$ (44.8 mg, 0.18 mmol) in water (10 ml) was added to the solution of Na(**2**)$(H_2O)_2$ (100 mg, 0.35 mmol) in methanol (10 ml). Then to the resulting mixture was added En (100 mg) and $NaClO_4$ (100 mg) in water (10 ml). The solution was kept at room temperature for 2 days. The violet plate-like crystals were filtered-off, washed with cold water and methanol, and dried in air. Yield: 57 mg (72%). The complex is soluble in hot water and has poor solubility in alcohols. Anal. Found: C, 21.9; H, 4.8; N, 22.3. Calc. for $C_{16}H_{44}N_{14}O_{14}Cl_3Ni_2$: C, 21.8; H, 5.0; N, 22.3%.

2.2.4. $[Mn(H_2O)_6][Mn(\mathbf{2})_3]_2(H_2O)_6$ (**6**)

A solution of $Mn(CH_3COO)_2(H_2O)_4$ (43.3 mg, 0.18 mmol) in water (10 ml) was added to the solution of Na(**2**)$(H_2O)_2$ (100 mg, 0.35 mmol) in CH_3OH (10 ml). The reaction mixture was allowed to stay in an open flask. After 14 days, dark violet blue cubic crystals formed; they were filtered-off, washed with cold water and ethanol, and dried in air. Yield: 41 mg (40%). The complex is soluble in water and methanol and has low solubility in ethanol. Anal. Found: C, 33.6; H, 5.8; N, 29.8. Calc. for $C_{48}H_{96}N_{36}O_{24}Mn_3$: C, 33.4; H, 5.6; N, 29.2%.

2.3. X-ray structure determination

The data for single crystals **2**–**6** were collected on an AXS P4 Bruker automatic diffractometer at room temperature using the standard procedure (Mo radiation, $\theta/2\theta$ scan mode, variable rate $V_{\min} = 3^\circ\ \min^{-1}$, $2^\circ < \theta < 25^\circ$). The structures were solved by direct methods. The full-matrix least-squares refinement was performed anisotropically for nonhydrogen atoms and isotropically for hydrogens. Some H atoms were localized in difference electron density syntheses; the others were placed theoretically. All structure solution and refinement calculations were carried out with SHELXS-97 software. The crystal data for the compounds and details of experiment are listed in Table 1; selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Syntheses and structures of **2**, **3**, and **4**

Since the nitrile group in **1** is activated by the nitronyl nitroxide fragment [8] and in view of the necessity to avoid acid media in nitroxide syntheses, Na(**2**) was obtained by addition of NaN_3 to **1** in DMF in the presence of 10 mol% NH_4Cl (Scheme 1). Under these conditions, the reaction of **1** with NaN_3 at 60 °C gave the target product after 2 h. The greenish blue color of the reaction mixture gradually changed to deep violet

Table 1
Crystal data and details of experiment

Formula	**3**	**4**	Na(**2**)(H_2O)$_2$	[En_2Ni(**2**)NiEn_2](ClO_4)$_3$	[Mn(H_2O)$_6$][Mn(**2**)$_3$]$_2$(H_2O)$_6$
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1$	$Pa\bar{3}$
Z	4	4	8	4	4
Unit cell					
a (Å)	6.788(1)	9.695(2)	20.500(3)	9.441(2)	19.899(2)
b (Å)	15.267(3)	10.346(2)	10.159(2)	13.472(3)	
c (Å)	11.539(2)	12.227(2)	13.386(2)	14.032(3)	
β (°)	101.31(3)	104.75(3)	104.987(3)	92.35(3)	
V (Å^3)	1172.6(4)	1186.0(4)	2693.0(7)	1783.2(6)	7879.8(16)
D_{calc} (g cm^{-3})	1.355	1.340	1.397	1.640	1.476
μ (mm^{-1})	0.101	0.100	0.138	1.359	0.570
I_{hkl} (means/unique)	2234/2051	2220/2090	11274/3872	6298/3811	1300/1300
R_{int}	0.0139	0.0401	0.2075	0.0251	0.0000
I_{hkl}/N	2051/215	2090/215	3872/472	3811/493	1300/196
Goodness-of-fit on F^2	1.022	0.936	1.091	1.026	0.967
R_1 [$I_{hkl} > 2\sigma(I)$]	0.0486	0.0584	0.0718	0.0420	0.0696
wR_2	0.1335	0.1192	0.1713	0.1029	0.1737
R_1	0.0755	0.1338	0.0809	0.0456	0.1760
wR_2	0.1540	0.1521	0.1866	0.1122	0.2322

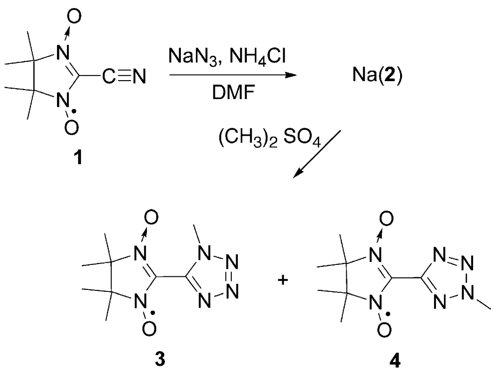
blue. The Na(**2**) product is well soluble in water, methanol, and ethanol but insoluble in THF, $CHCl_3$, and acetone. The salt does not melt below 200 °C; at ~ 218 °C it is transformed into a yellow orange substance.

Methylation of **2** by $(CH_3)_2SO_4$ in water led to the formation of a mixture of **3** and **4**. Attempts to separate isomers **3** and **4** chromatographically on silica gel or aluminum oxide failed. Crystallization of a mixture of **3** and **4** from heptane with CH_2Cl_2 gave perfect crystals differing in shape, which were separated manually and defined by structural analysis (Figs. 1 and 2, Table 2). The mass ratio of isomers **3**/**4** was ~4/1.

Structure investigation of **3** and **4** showed that the variation of the position of the CH_3 group in the tetrazole ring considerably affects the angle between the planes of the CN_2 fragment of the imidazoline cycle and tetrazole (in Table 2, this angle is designated as ∠CN_2–tz). The angle is 51.2° in molecules **3** and 16.7° in **4**. The remarkable decrease in the angle from **3** to **4** is evidently explained by the disappearance of steric

Table 2
Selected bond lengths (Å) and angles (°)

	3	**4**	Na(**2**)(H_2O)$_2$		[En_2Ni(**2**)NiEn_2](ClO_4)$_3$		[Mn(H_2O)$_6$][Mn(**2**)$_3$]$_2$(H_2O)$_6$	
Bond lengths (Å)								
M–O_w			2.315(3)	2.424(2)			2.23(3)	
			2.410(2)	2.578(3)			2.14(2)	
M–O_L			2.473(2)	2.394(2)	2.117(5)	2.108(5)		2.155(8)
			2.391(2)	2.385(2)				
M–N_L			2.477(2)	2.435(2)	2.071(6)	2.069(5)		2.182(9)
			2.483(2)	2.421(2)				
M–N_{En}					2.097(5)	2.084(7)		
					2.098(6)	2.114(6)		
					2.112(6)	2.087(7)		
					2.110(6)	2.100(6)		
N–O	1.270(2)	1.267(3)	1.270(2)	1.271(2)	1.282(7)	1.308(7)		1.286(9)
	1.277(2)	1.283(3)	1.282(2)	1.287(2)				1.261(11)
–O···O–	3.193	4.289	3.865	4.013				3.050
Bond angles (°)								
∠O_L–M–N_L			70.39(6)	72.10(7)	85.3(2)	85.6(2)		82.1(3)
			74.55(6)	75.39(7)				
∠N_{En}–M–N_{En}					82.7(2)	81.9(3)		
					82.5(2)	81.3(3)		
∠N–O–M			117.2(1)	122.0(1)	127.2(4)	129.2(4)		124.1(6)
			135.5(1)	134.4(1)				
∠CN_2–tz	51.2(2)	16.7(3)	18.3(2)	18.5(2)	1.0(3)			23.5(4)



Scheme 1.

hindrances due to the transition of the CH_3 group into the second position of the tetrazole cycle. In the structure of **3** one can isolate centrosymmetric pairs of molecules for which the shortest distance between the oxygen atoms of the NO groups is 3.193 Å. These pairs, in turn, are linked into layers by weak contacts between the remaining O atoms and the H atoms of the methyl groups of the imidazoline cycle (O· · ·H, 2.55 Å) (Fig. 2(a)). In solid **4**, one can also isolate centrosymmetric pairs with contacts between the O atom and the N atoms of the tetrazole fragment of the neighboring molecule equal to 3.213 and 3.359 Å. The other O atom forms a weak hydrogen bond with the H atom of the methyl group of the tetrazole cycle (2.43 Å), leading to zigzag chains (Fig. 2(b)).

In the structure of $Na(\mathbf{2})(H_2O)_2$, the two crystallographically independent sodium atoms have a distorted octahedral environment formed by the O atoms of two water molecules, two N atoms of the tetrazole cycles, and two O atoms of the NO groups of the two anions **2** (Table 2). Each anion **2** forms with the Na atom, a six-membered metallocycle with the Na atom, where the ONaN angle is 70.39–75.39°. The average $Na-O_w$, $Na-O_{NO}$, and $Na-N_{tz}$ bond lengths equal 2.432, 2.411, and 2.454 Å, respectively. As in **4**, the CN_2–tz angle is 18.4° due to the absence of steric hindrances. The paramagnetic anions **2** act as bridges connecting the sodium atoms into chains linked into double layers (Fig. 3) by H bonds between the N_{tz} atoms and the water molecules from the neighboring chains ($N_{tz}\cdots O_w$, 2.795–2.992 Å).

3.2. Structures of complexes

Structure analysis of $[En_2Ni(\mathbf{2})NiEn_2](ClO_4)_3$ confirmed that the paramagnetic ligand **2** performs the symmetric bridging function (Fig. 4). In the binuclear cation $[En_2Ni(\mathbf{2})NiEn_2]^{3+}$, the Ni atom is surrounded by a distorted octahedron formed from the donor atoms of **2** and the N atoms of the two ethylenediamine ligands. The average distances are: $Ni-N_{En}$, 2.100 Å; $Ni-N_{tz}$, 2.070 Å; and Ni–O, 2.112 Å. The participation of the bridging anion **2** in the formation of two chelate cycles leads to almost complete coplanarity of the heterocycles ($\angle CN_2$–tz is up to 1.0°). The binuclear

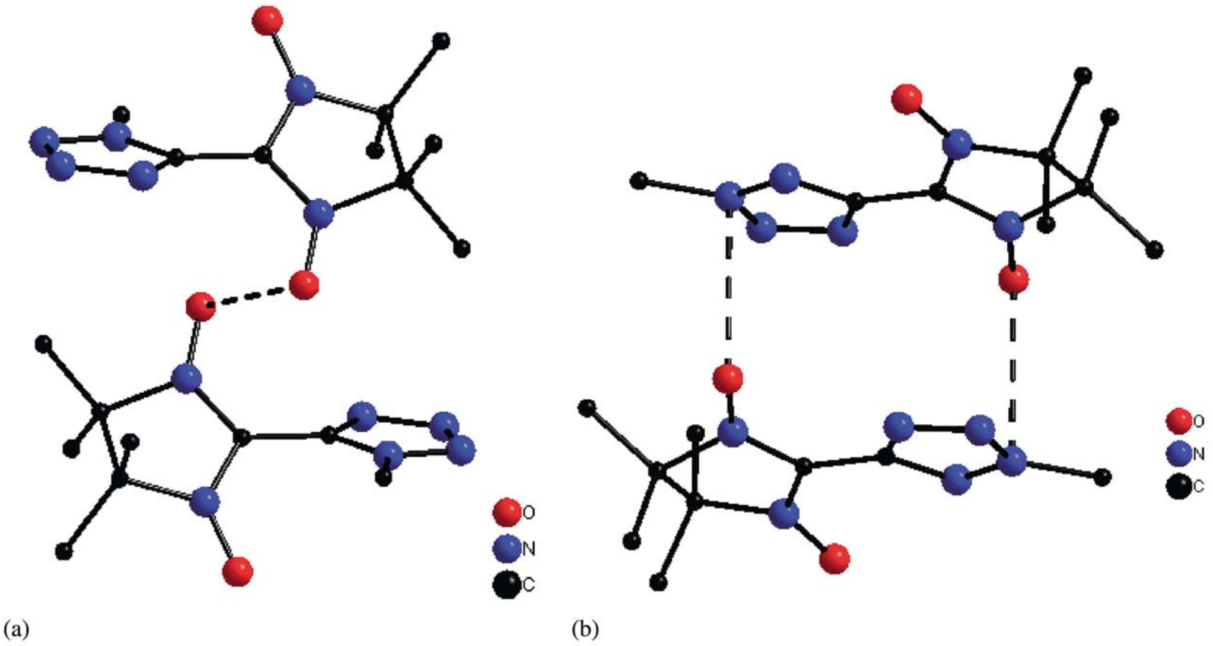


Fig. 1. Atomic numbering scheme in the centrosymmetric pairs of molecules in **3** (a) and **4** (b).

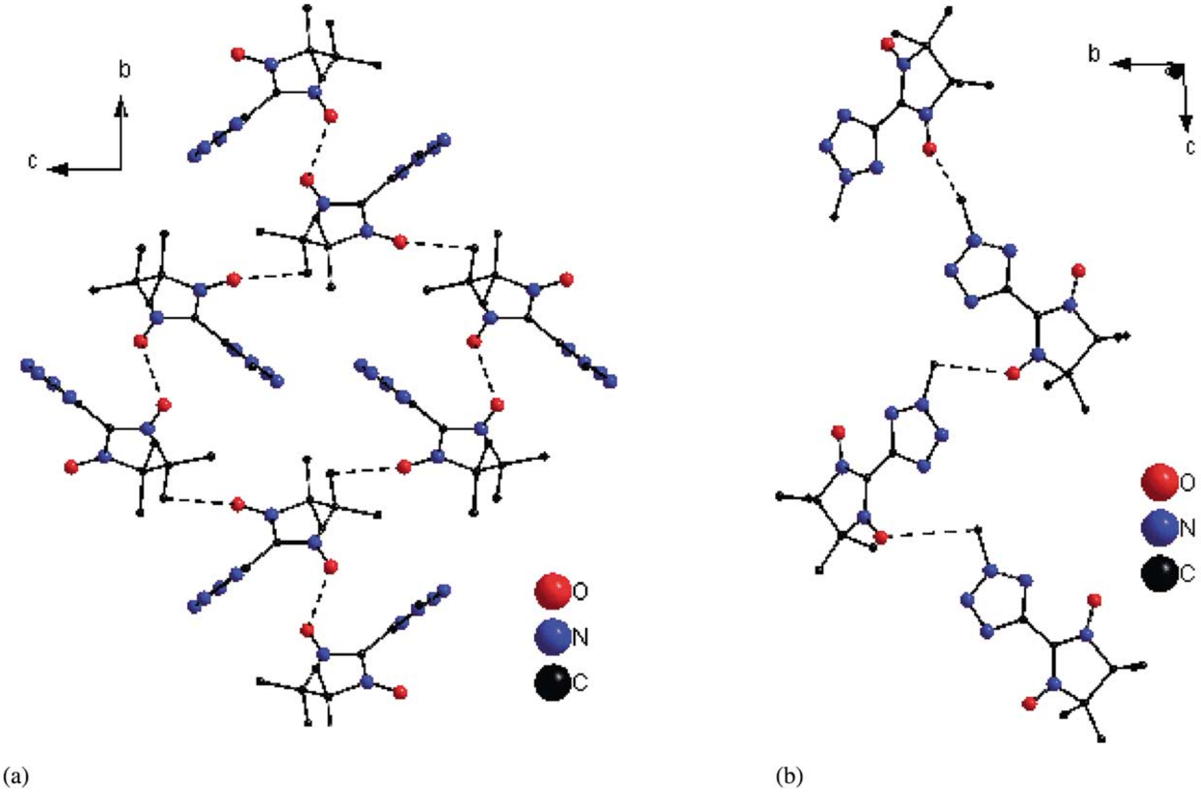


Fig. 2. Molecular packing in **3** (a) and **4** (b).

cations and the ClO_4 anions in solid $[En_2Ni(\mathbf{2})NiEn_2](ClO_4)_3$ are linked by H bonds between the O atoms of the perchlorate anions and En coordinated by the NH_2 groups into layers (Fig. 5).

As opposed to $[En_2Ni(\mathbf{2})NiEn_2](ClO_4)_3$, in solid $[Mn(H_2O)_6][Mn(\mathbf{2})_3]_2(H_2O)_6$ all paramagnetic ligands are cyclic bidentate ligands forming a nearly symmetric octahedral environment of the central atom in

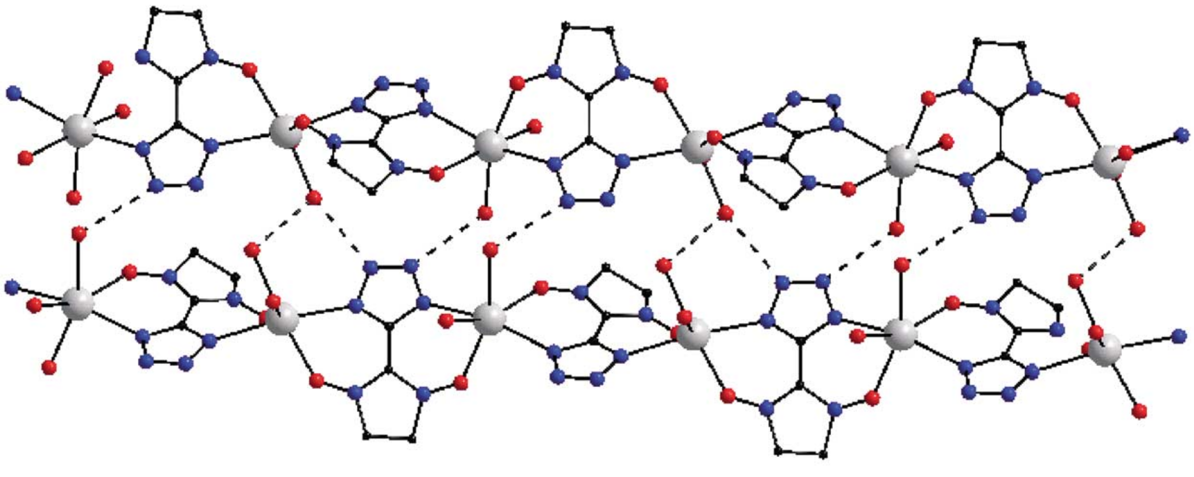


Fig. 3. Layer in the structure of $Na(\mathbf{2})(H_2O)_2$.

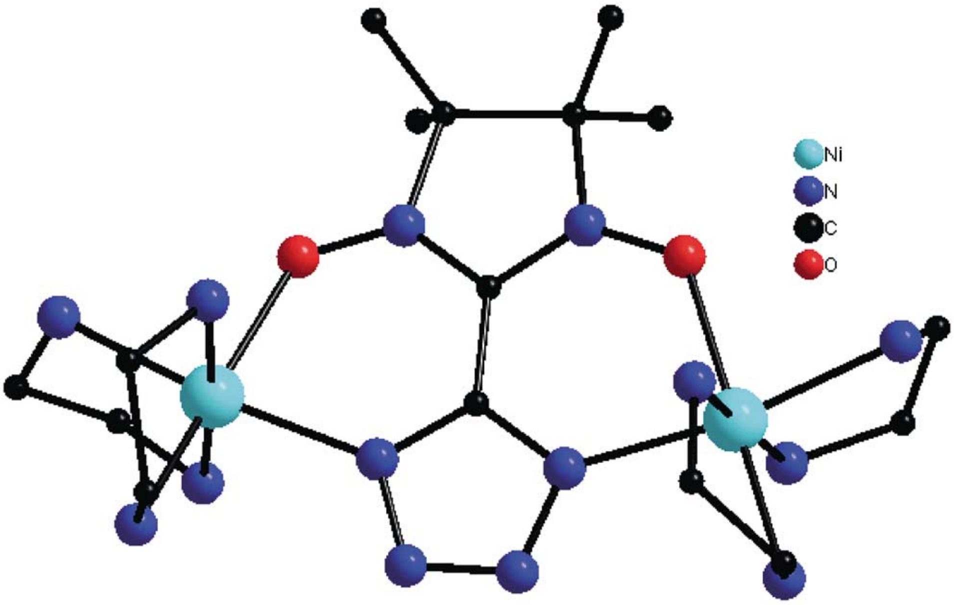


Fig. 4. Structure of the $[En_2Ni(\mathbf{2})NiEn_2]^{3+}$ complex cation.

$[Mn(\mathbf{2})_3]^-$ complex anions with Mn–O and Mn–N distances equal to 2.16 ± 0.02 Å and with the chelate angle equal to 82.1°. The environment of the central atom in the $[Mn(H_2O)_6]^{2+}$ coordination cations is also close to octahedral (Fig. 6). The complex cations and the anions are bound into a diamond-like framework (Fig. 6) by tight H bonds between the coordinated water molecules, the nitroxyl groups, and the N atoms in the third and fourth positions of the tetrazole ring.

Thus, procedures for the synthesis of nitronyl nitroxides with a tetrazole cycle as substituent have been worked out. The paramagnetic anion **2**, which is

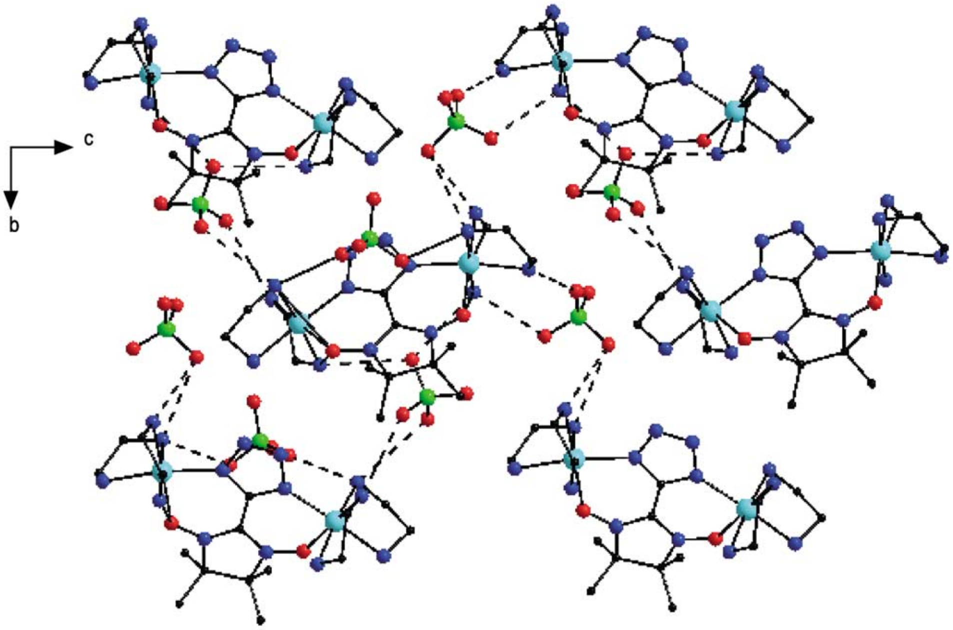


Fig. 5. Projection of a layer in the structure of $[En_2Ni(\mathbf{2})NiEn_2](ClO_4)_3$.

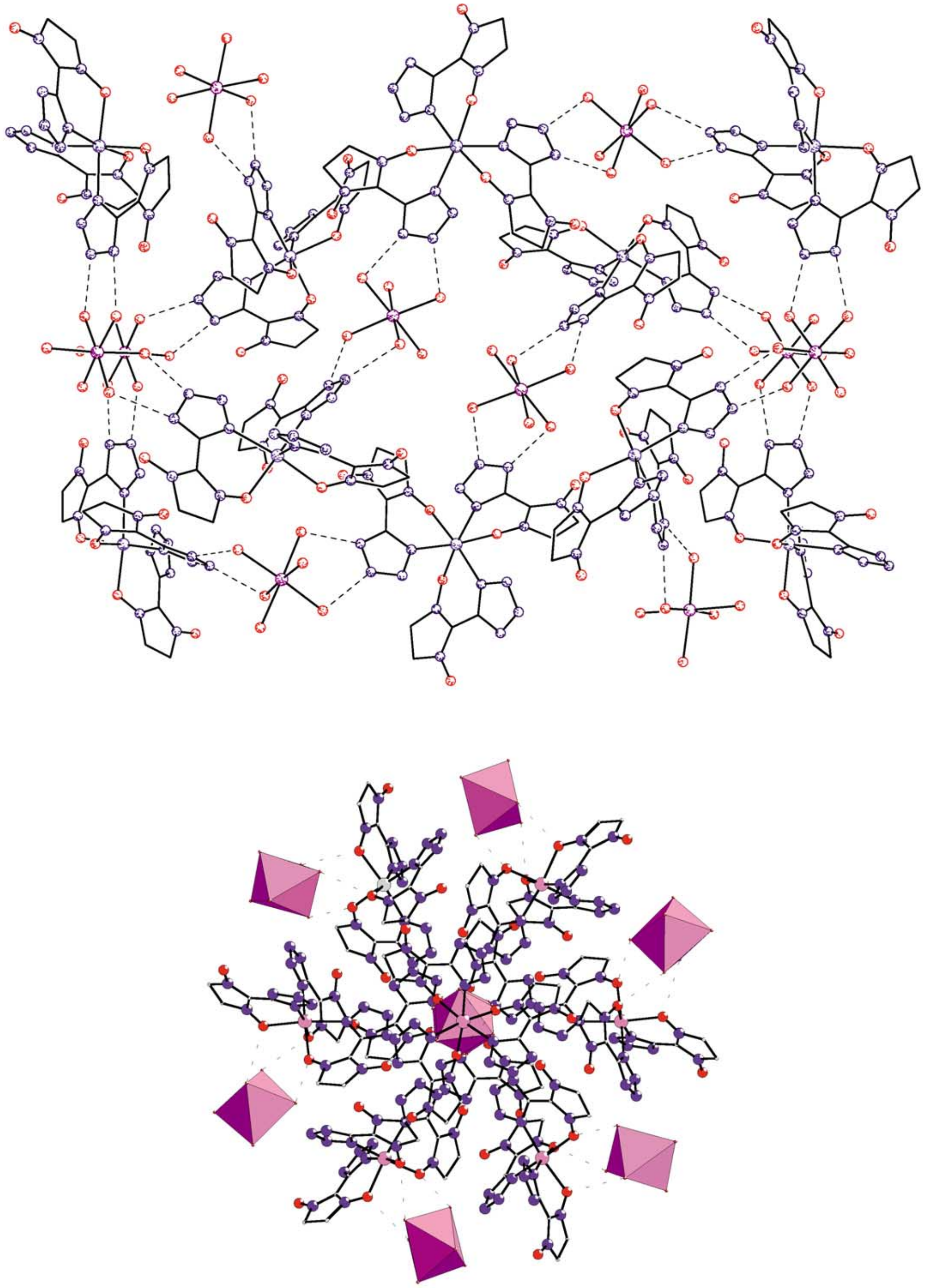


Fig. 6. Fragment of framework in the structure of $[Mn(H_2O)_6][Mn(\mathbf{2})_3]_2(H_2O)_6$.

symmetric relative to the donor groups, tends to perform the bridging function in reactions with metal anions, which favors the formation of highly dimensional heterospin structures. We intend to synthesize other highly dimensional heterospin complexes with **2**–**4** and study their magnetic properties.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 195775 for **4**, 195776 for $[En_2Ni(\mathbf{2})NiEn_2](ClO_4)_3$ (**5**), 195777 for Na(**2**), 195778 for **3**, and 195779 for $[Mn(H_2O)_6][Mn(\mathbf{2})_3]_2(H_2O)_6$ (**6**). Copies of this information may be obtained free of charge 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://ccdc.cam.ak.uk).

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