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Synthesis, Crystal Structures, and Characterization of a New Substituted 1,2,4-Triazole and Its Two Co(II)/Mn(II) Complexes[1]

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Abstract—A new triazole-substituted ligand H_2L (H_2Trza = 3-amino-1*H*-1,2,4-triazole-5-acetate) and its two new isomorphic compounds $[M(HTrza)_2(H_2O)_2] \cdot 2H_2O$ (Co(**I**) and Mn(**II**)) have been synthesized and characterized structurally. Their X-ray crystal structures (CIF files CCDC nos. 906893 for **I** and 906892 for **II**) show that H_2L belongs to a tetragonal system; space group $P4_3$ with $a = b = 5.0445(13)$, $c = 27.054(10)$ Å; $Z = 4$. Complex I belongs to a monoclinic system; space group $P2_1/n$ with $a = 7.6543(8)$, $b = 7.3453(8)$, $c = 13.6283(14)$ Å; $\beta = 91.5990(10)°$, $Z = 2$. Complex **II** belongs to a triclinic system; space group $P\bar{1}$ with $a = 6.8550(15)$, $b = 8.0630(18)$, $c = 15.173(4)$ Å; $\alpha = 84.794(4)°$, $\beta = 79.005(3)°$, $\gamma = 73.779(4)°$, $Z = 2$. X-ray analysis demonstrates that compound H_2L is found to contain a H_2Trza and a lattic water molecule; complexes **I** and **II** are discrete mononuclear species. The central Co(**II**) and Mn(**II**) atoms exhibit octahedral coordinations, type 4 + 2. In two compounds, the coordination entities are further organized via hydrogen-bonding interactions to generate uniform supramolecular networks. Thermal stabilities of two compounds were examined by thermogravimetric analysis.

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INTRODUCTION

The design and synthesis of coordination polymers have been flourishing in recent years because of their diverse architectures and useful properties, such as catalysis, optics, ferroelectrics, magnetism, ion change and gas sorption catalysis [1–4]. A large number of compounds with intricate structures ranging from 1D chain to 3D networks have been obtained by selecting of organic ligands [5–8]. Most commonly used organic ligands are polycarboxylate and polypyridines because the former can exhibit versatile coordination modes, while the latter can afford more predictable coordination modes. In recent years, 1,2,4-triazole, in particular, its derivatives gain more and more interest as ligands to bridge metal ions because of their potential $\mu_{1,2}$-, $\mu_{2,4}$-, $\mu_{1,2,4}$-bridging fashions. Many triazole-based compounds have been reported to date [9–12]. Therefore, 3-amino-1*H*-1,2,4-triazole ($AmTAZ^-$), as a not widely used ligand in the field of coordination polymers, is chosen [13]. And the $AmTAZ^-$ ligand was derived from the decarboxylation of 3-amino-1,2,4-triazole-5-carboxylic acid in the solvothermal process [14]. The development of new ligand systems is continuously an important aspect for the chemistry of coordination polymers.

In order to extend our research in this field, we have synthesised 3-amino-1*H*-1,2,4-triazole-5-acetate (H_2Trza) as a functional building block on account of the following considerations: (a) H_2Trza possesses a carboxyl group that may be deprotonated; (b) it also possesses an amino functional group; (c) it is a flexible ligand allowing the rotation of acetate group. To our knowledge, no compound with this ligand has been reported. In the present paper, we report the syntheses, crystal structures and thermal stabilities of two Co(II)/Mn(II)-complexes with H_2L, whose structures were characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction analysis.

EXPERIMENTAL

Materials and method. All reagents used in the syntheses were of analytical grade were used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 cm^{-1}) were recorded by using KBr pellet on an AvatarTM 360 E.S.P. IR spectrometer. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo radiation ($\lambda = 0.71073$ Å). The thermogravimetric analyses (TGA) were performed

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for H_2L, **I**, **II**

Paramrter	Value		
	H_2L	**I**	**II**
Formula weight	160.14	413.23	409.24
Temperature, K	296(2)	296(2)	296(2)
Crystal system	Tetragonal	Monoclinic	Triclinic
Space group	$P4_3$	$P2_1/n$	$P\bar{1}$
a, Å	5.0445(13)	7.6543(8)	6.8550(15)
b, Å		7.3453(8)	8.0630(18)
c, Å	27.054(10)	13.6283(14)	15.173(4)
α, deg			84.794(4)
β, deg		91.5990(10)	96.481(2)
γ, deg			73.779(4)
Volume, Å^3; Z	688.4(3)	765.93(14); 2	789.8(3); 2
ρ_{calcd}, Kg/m^3	1.545	1.792	1.721
Reflections collected/ unique (R_{int})	3722/1198 (0.0451)	4143/1638 (0.0185)	4391/3111 (0.0328)
Goodness-of-fit on F^2	1.065	0.943	1.010
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0455$	$R_1 = 0.0294$	$R_1 = 0.0548$
	$wR_2 = 0.1071$	$wR_2 = 0.1082$	$wR_2 = 0.1196$
R indices (all data)	$R_1 = 0.0520$	$R_1 = 0.0329$	$R_1 = 0.0862$
	$wR_2 = 0.1105$	$wR_2 = 0.1158$	$wR_2 = 0.1414$
Largest diff. peak and hole, e Å^{-3}	0.307 and −0.361	0.279 and −0.303	0.362 and −0.421

on a STA449C integration thermal analyzer in flowing N_2 with a heating rate of 10°C/min.

Synthesis of H_2Trza was carried out by intramolecular condensation of the malonyl derivative of aminoguanidine bicarbonate in alkaline medium [15]. The colorless crystals of H_2Trza were recrystallized from methanol in 45% yield.

For $C_4H_8N_4O_3$

anal. calcd., %:	C, 33.80;	H, 4.25;	N, 39.42.
Found, %:	C, 33.36;	H, 4.71;	N, 39.07.

Infrared spectrum (KBr; ν, cm^{-1}): 3396 s, 28935 w, 1700 s, 1573 m 1374 m, 1284 m, 1031 w, 706 w.

Synthesis of $[Co(Htrza)_2(H_2O)_2] \cdot H_2O$ (I) was carried out by the adding $CoCl_2 \cdot 6H_2O$ (0.1 mmol, 24 mg) to a 20 mL ethanol solution of H_2Trza (0.2 mmol, 29 mg). The mixture was stirred for 4 h and then filtered; the clear light red filtrate was allowed to stand at room temperature in the dark for two weeks. Red crystals of **I** were obtained in a yield of 42%.

For $C_8H_{18}N_8O_8Co$

anal. calcd., %:	C, 23.25;	H, 4.39;	N, 27.12.
Found, %:	C, 23.31;	H, 4.34;	N, 27.24.

Infrared spectrum (KBr; ν, cm^{-1}): 3425 s, 2140 w, 1678 s, 1618 s, 1421 m, 1084 w, 833 w, 715 m.

Synthesis of the $[Mn(HTrza)_2(H_2O)_2] \cdot 2H_2O$ (II) was carried out by the adding $MnCl_2 \cdot 4H_2O$ (0.1 mmol, 20 mg) to a 20 mL ethanol solution of H_2Tza (0.2 mmol, 30 mg). The mixture was stirred for 4 h and then filtered; the clear colourless filtrate was allowed to stand at room temperature in the dark for two weeks. Colourless crystals of **II** were obtained in a yield of 39%.

For $C_8H_{18}N_8O_8Mn$

anal. calcd., %:	C, 23.46;	H, 4.43;	N, 27.38.
Found, %:	C, 23.39;	H, 4.41;	N, 27.26.

Infrared spectrum (KBr; ν, cm^{-1}): 3411 s, 2369 w, 1671 s, 1558 s, 1392 m, 1118 w, 828 w, 712 m.

X-ray crystallography. Single crystal X-ray diffractions analysis of the compounds H_2L, **I**, **II** was carried out. Single crystals of these compounds were put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using φ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97 [16]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [17]. The final agreement factor values are R = 0.0455, wR = 0.1071 ($w = 1/[\sigma^2(F_o)^2 +$

Table 2. Selected bond distances and angles for H_2L, **I**, **II**

Bond	*d*, Å	Bond	*d*, Å
		H_2L	
C(1)–O(2)	1.242(4)	C(3)–N(1)	1.377(4)
C(1)–O(1)	1.264(4)	C(4)–N(4)	1.326(4)
C(3)–N(2)	1.289(4)	C(4)–N(3)	1.334(4)
N(2)–N(3)	1.389(4)	C(4)–N(1)	1.360(4)
		I	
Co(1)–N(1)	2.094(17)	Co(1)–O(1)	2.1144(1)
Co(1)–O(3)	2.107(1)		
		II	
Mn(1)–N(1)	2.241(3)	Mn(1)–O(2)	2.183(3)
Mn(2)–N(5)	2.175(3)	Mn(2)–O(5)	2.179(3)
Mn(1)–O(1)	2.161(3)	Mn(2)–O(4)	2.258(3)
Angle	ω, deg	Angle	ω, deg
		H_2L	
N(3)C(4)N(1)	107.0(3)	N(4)C(4)N(1)	126.6(3)
O(2)C(1)O(1)	124.7(3)	N(1)C(3)C(2)	123.6(3)
C(3)N(2)N(3)	106.2(3)	C(4)N(1)C(3)	106.5(3)
O(2)C(1)C(2)	119.5(3)	N(4)C(4)N(3)	126.4(3)
N(2)C(3)N(1)	110.8(3)	N(2)C(3)C(2)	125.6(3)
O(1)C(1)C(2)	115.8(3)	C(3)C(2)C(1)	113.9(3)
		I*	
N(1)Co(1)O(3)	86.98(6)	$N(1)^{\#1}$Co(1)O(1)	93.98(6)
C(1)N(1)Co(1)	129.84(16)	C(2)N(1)Co(1)	123.40(13)
O(3)Co(1)O(1)	89.08(6)		
		II	
N(5)Mn(2)O(4)	91.19(12)	O(1)Mn(1)N(1)	89.37(1)
O(1)Mn(1)O(2)	86.41(1)	O(5)Mn(2)O(4)	93.22(13)
O(2)Mn(1)N(1)	95.37(11)	N(5)Mn(2)O(5)	95.40(11)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+2, -y, -z+2$.

$(0.0400P)^2 + 0.4325P]$, where $P = (F_o^2 - 2F_c^2)/3)$, $S = 1.065$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.307$ and $(\Delta\rho)_{mix} = -0.361$ e/Å^3 for H_2L, $R = 0.0294$, $wR = 0.1082$ ($w = 1/[\sigma^2(F_o)^2 + (0.1000P)^2 + 0.0000\underline{P}]$, where $P = (F_o^2 - 2F_c^2)/3)$, $S = 0.943$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.279$ and $(\Delta\rho)_{mix} = -0.303$ e/Å^3 for **I**, and $R = 0.0548$, $wR = 0.1196$ ($w = 1/[\sigma^2(F_o)^2 + (0.0600P)^2 + 0.0000P]$, where $P = (F_o^2 - 2F_c^2)/3)$, $S = 1.010$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.362$ and $(\Delta\rho)_{mix} = -0.421$ e/Å^3 for **II**. Table 1 shows crystallographic crystal data of compounds H_2L, **I**, **II**. Selected bond lengths and angles are listed in Table 2. The atomic coordinates and other parameters of complexes **I** and **II** have been deposited with the Cambridge Crystallographic Data Center (CCDC nos. 906893 (**I**) and 906892 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

RESULTS AND DISCUSSION

The molecular structure of H_2L is depicted in Fig. 1a. The compound **I** is found to contain one H_2Trza molecule and one lattic water molecule. The amino group and triazole ring is nearly coplanar. The corresponding torsion angles of N(4)–C(4)–N(3)–N(2) and N(4)–C(4)–N(1)–C(3) are 179.2(3)° and −179.1(3)°, respectively. The methylene and triazole ring is coplanar. And the torsion angles between the carboxy group and triazole ring (O(1)–C(1)–C(2)–C(3) and O(2)–C(1)–C(2)–C(3)) are 170.0(3)° and −11.2(5)°, respectively. There are significant intermo-

Table 3. Geometric parameters of hydrogen bonds for compounds H_2L, **I**, **II***

D–H···A	Disnance, Å			Angle DHA, deg
	D–H	H···A	D···A	
		H_2L		
O(1)–H(1*w*)···O(2)$^{\#1}$	0.89	1.88	2.766(4)	171.4
O(1)–H(2*w*)···O(3)$^{\#2}$	0.78	2.02	2.778(4)	163.7
N(4)–H(4*B*)···N(2)$^{\#3}$	0.86	2.11	2.959(5)	171.5
N(4)–H(4*A*)···O(2)$^{\#4}$	0.86	2.10	2.899(5)	153.6
N(1)–H(1)···O(3)$^{\#4}$	0.86	1.80	2.656(4)	176.4
		I		
O(4)–H(2*w*)···O(1)$^{\#2}$	0.75(4)	2.08(4)	2.824(2)	170(3)
O(4)–H(1*w*)···N(3)	0.80(3)	2.12(3)	2.910(3)	171(3)
O(3)–H(3*w*)···O(2)$^{\#3}$	0.87(3)	1.89(3)	2.749(2)	170(2)
O(3)–H(4*w*)···O(4)$^{\#4}$	0.82	1.95	2.741(2)	161.2
N(4)–H(4*B*)···O(4)$^{\#3}$	0.86	2.07	2.886(3)	158.2
N(4)–H(4*A*)···O(1)$^{\#1}$	0.86	2.23	2.989(2)	146.8
N(2)–H(2)···O(2)$^{\#5}$	0.86	2.09	2.883(2)	152.3
		II		
O(8)–H(4*w*)···O(6)$^{\#3}$	1.04	1.69	2.735(4)	177.6
O(4)–H(4)···N(2)	0.82	2.04	2.849(4)	166.9
N(8)–H(8*B*)···O(5)	0.86	2.50	3.210(5)	140.3
N(6)–H(6)···O(3)$^{\#4}$	0.86	1.87	2.704(4)	163.8
N(4)–H(4*B*)...O(2)	0.86	2.48	3.238(4)	148.0
N(4)–H(4*A*)···O(6)$^{\#3}$	0.86	2.20	3.023(5)	160.6
N(3)–H(3*C*)···O(8)	0.86	2.02	2.856(4)	162.4
O(8)–H(3*w*)···O(5)	0.87	1.91	2.765(4)	170.6
O(7)–H(2*w*)···O(2)	1.07	2.63	3.390(4)	127.7
O(7)–H(2*w*)···O(3)	1.07	1.83	2.797(4)	148.3
O(7)–H(1*w*)···O(2)$^{\#5}$	0.77	2.14	2.896(4)	169.7
O(4)–H(3)···O(8)$^{\#6}$	0.71	2.10	2.806(4)	174.7
O(1)–H(2)···N(7)$^{\#1}$	0.71	2.11	2.795(4)	163.8
O(1)–H(1)···O(7)$^{\#7}$	0.95	1.81	2.742(4)	170.0

* Symmetry codes: $^{\#1}$ $-x+1, -y+1, z-1/2$; $^{\#2}$ $x+1, y, z$; $^{\#3}$ $-x+1/2, y-1/2, z+1/2$; $^{\#4}$ $x+1/2, -y+3/2, z$ for H_2L; $^{\#1}$ $-x+2, -y, -z+2$; $^{\#2}$ $x-1/2, -y+1/2, z-1/2$; $^{\#3}$ $x+1, y, z$; $^{\#4}$ $-x+3/2, y+1/2, -z+3/2$; $^{\#5}$ $x+1/2, -y+1/2, z-1/2$ for **I**; $^{\#1}$ $-x+1, -y, -z+2$; $^{\#3}$ $-x+1, -y+1, -z+1$; $^{\#4}$ $-x+1, -y+1, -z+2$; $^{\#5}$ $-x, -y+1, -z+2$; $^{\#6}$ $-x+1, -y, -z+1$; $^{\#7}$ $x, y-1, z$ for **II**.

lecular contacts in the structure of the compound. The intermolecular hydrogen bonds occur between the compounds, via the uncoordinated water molecules, amino group of H_2Trza, and carboxy group. The detailed hydrogen bond parameters are listed in Table 3. Thus, a 3D supramolecular network is formed by intermolecular interactions (Fig. 1b).

Compound **I** exhibits discrete mononuclear species. Compound **I** contains a $[Co(HTrza)_2(H_2O)_2]$ molecule and two solvent water molecules. The $[Co(HTrza)_2(H_2O)_2]$ unit consists of one Co^{2+} ion, two $HTrza^-$ ligands, two coordinated water molecules (Fig. 2a). The Co^{2+} ion is located on an inversion center and adopts a distorted octahedral coordination arrangement, where the equatorial coordination comes from two nitrogen atoms and two oxygen atoms from two H_2Trza ligands, the axial position is occupied by two oxygen atoms from coordinated water molecules. The bond lengths of Co(1)–O(1) and Co(1)–O(3) are equal to 2.1144(13) and 2.1076(15) Å,

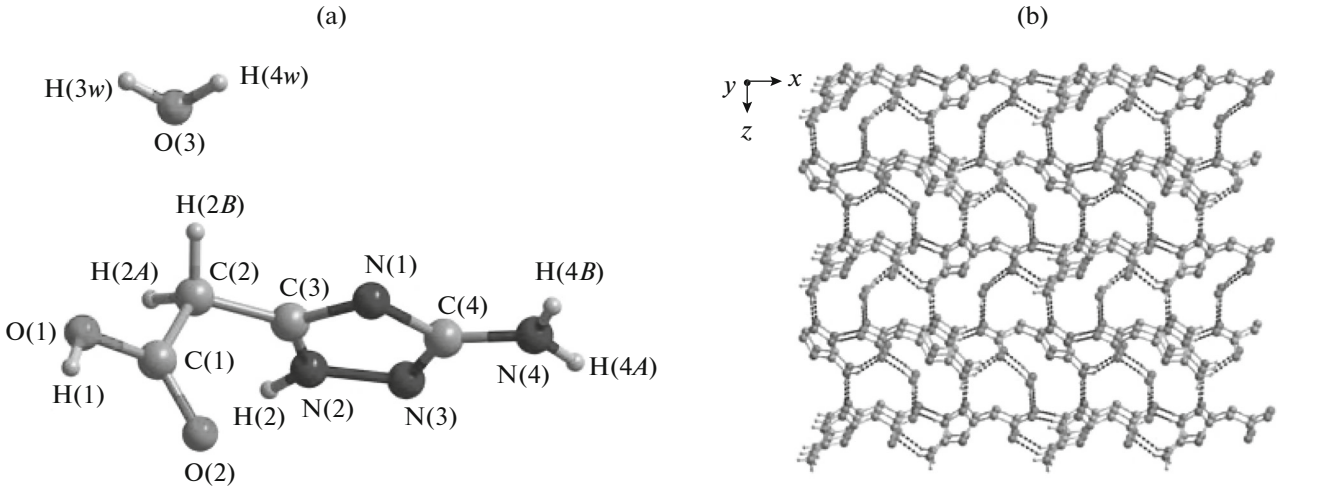

Fig. 1. Crystal structure of H_2L (a); 3D supramolecular structure of H_2L (b).

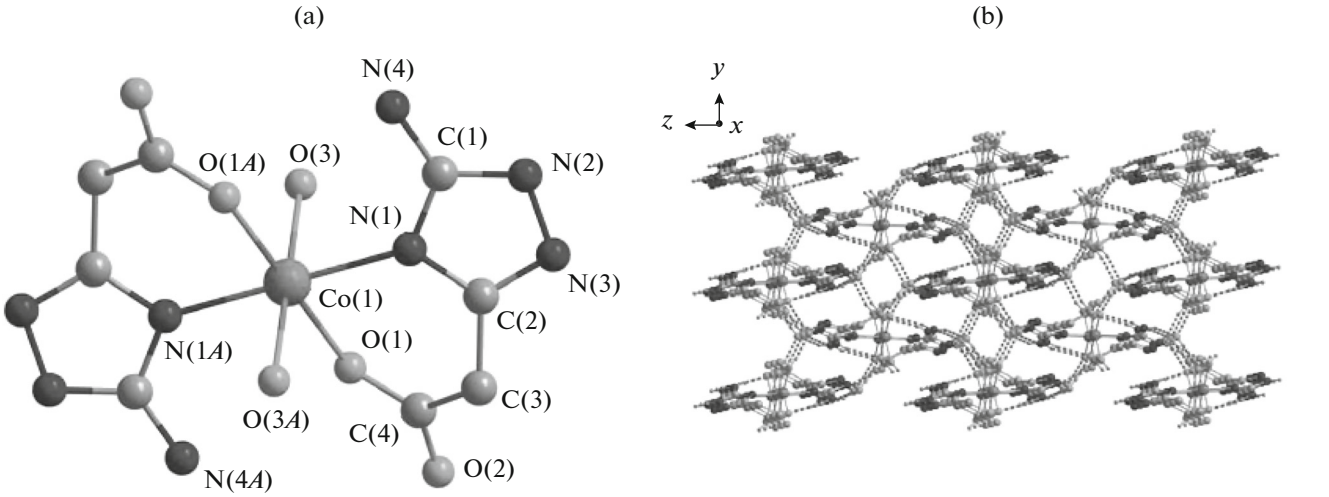

Fig. 2. The coordination environment of Co^{2+} ion in **I** (a); hydrogen bonds interactions of **I** (b).

respectively. The bond lengths of Co(1)–N(1) is equal to 2.0944(17) Å. The angle, such as: N(1)Co(1)O(1) (86.02(6)°), is close to the ideal values of 90°. Each H_2Trza ligand binds to the metal center through the 4-nitrogen atom in 1,2,4-triazole ring and acetate group O atom, while the amino group is free from coordination. The crystal packing of **I** is shown in Fig. 2b. Complex molecules are linked together by a system of hydrogen bonds. Classic hydrogen bonds O–H···N, O–H···O, and N–H···O link the above discrete molecules into a 3D network.

A view of the molecular structure of **II** is depicted in Fig. 3a. Compared with **I**, compound **II** consists of two crystallographically independent mononuclear Mn(1) and Mn(2) complexes with the same six coordination core of N_2O_4 and octahedral coordination geometry. Due to their structural isomorphism, the corresponding bond distances and angles of Mn(1) and Mn(2) complexes are not significantly different. And single crystal X-ray analysis reveals that compounds **I** and **II** are isostructural, and hence structure **II** is not detailly discussed. Compounds **I** and **II** have the same hydrogen bond interactions. Therefore, further studies of the crystallographic data have shown that the discrete mononuclear species are further packed into a 3D supramolecular structure (Fig. 3b) through intermolecular hydrogen bonding interactions.

TGA were carried out under N_2 atmosphere to examine the thermal stability of complexes **I** and **II** and the results are shown in Fig. 4. For complex **I**, the two lattice water molecules and one coordination water molecule are lost in a continuous fashion from 115° to 168°C (obsd. 11.7%, calcd. 13.3%), and further weight loss was observed at about 200°C, owing to the decomposition of **I**. For complex **II**, the lattice water and coordination water molecules are lost in a continuous fashion from 108° to 164°C (obsd. 12.25%, calcd.

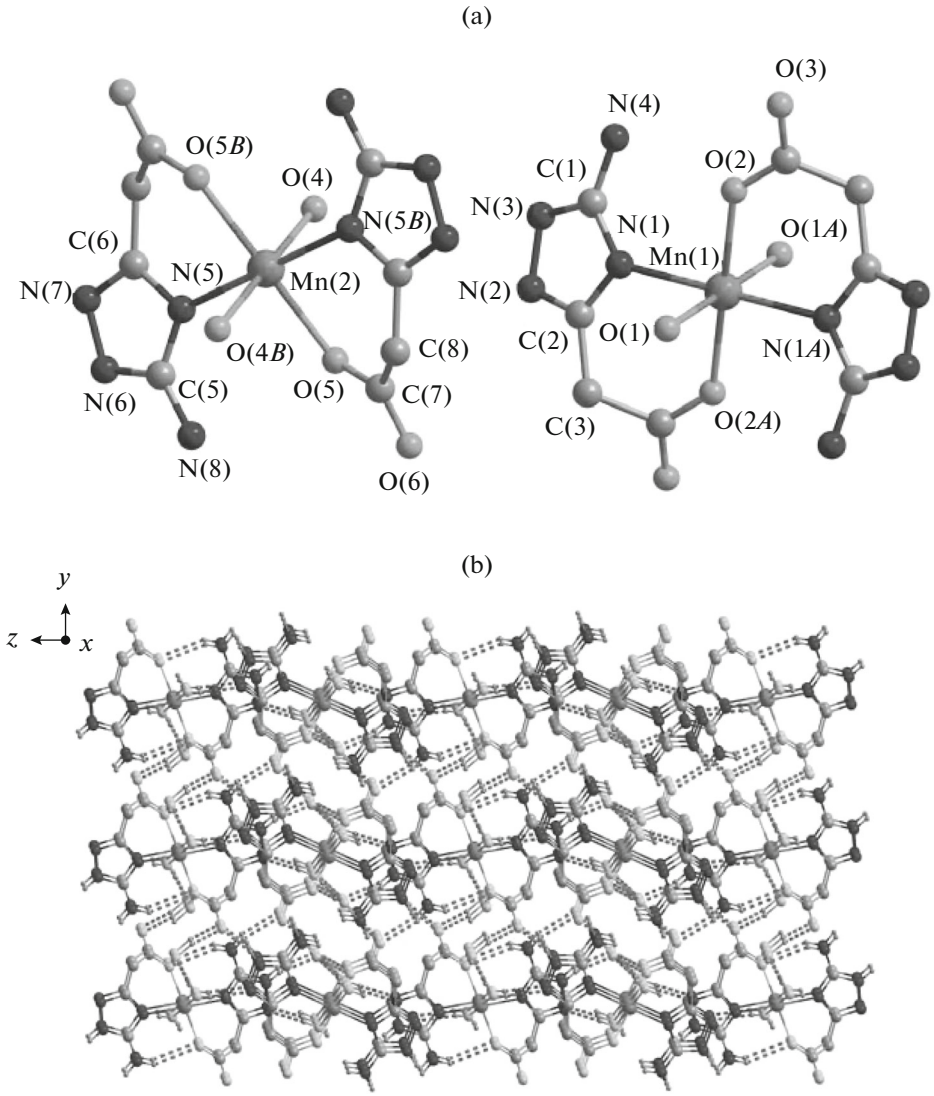

Fig. 3. The coordination environment of Mn^{2+} ions in **II** (a); hydrogen bonds interactions of **II** (b).

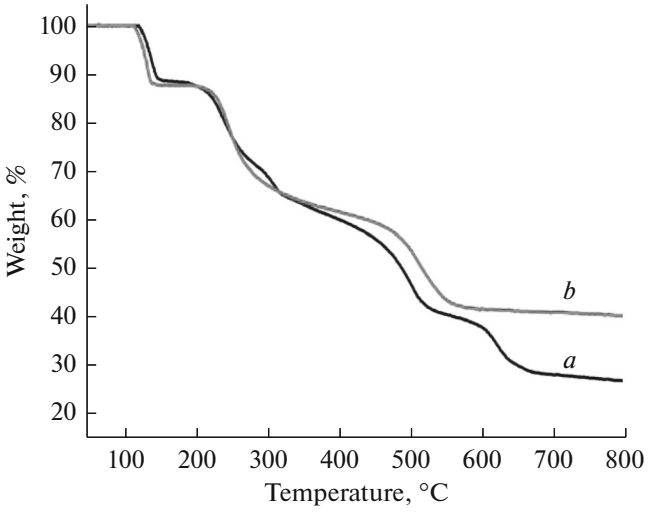

Fig. 4. The TGA diagrams of compounds **I** (*a*) and **II** (*b*).

13.19%) and the decomposition of the residue was observed at 211°C.

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