

Synthesis and Structural Characterization of Two New Copper(II) Complexes with 3-Oxapentane-1,5-Diamine Using Different Molar Ratio¹

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Abstract—The reactions of copper(II) nitrate with 3-oxapentane-1,5-diamine (Oda) were investigated under different molar ratio. In the case of a 1 : 1 molar ratio of copper(II) nitrate and Oda, the mononuclear complex $[\text{Cu}(\text{Oda})(\text{NO}_3)_2]$ (**I**) was obtained. In contrast, the treatment of copper(II) nitrate with twice Oda afforded inorganic polymer $\{[\text{Cu}(\mu\text{-Oda})(\text{Oda})] \cdot (\text{NO}_3)_2\}_n$ (**II**). The molecular structures of the two new complexes were determined from the elemental analyses, IR spectra and single-crystal X-ray diffraction (CIF files CCDC nos. 828193 (**I**) and 828018 (**II**)). Two Cu(II) complexes were both five-coordinated and forming a distorted square-base pyramidal geometry. Two complexes are stabilized by the intermolecular hydrogen-bond.

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INTRODUCTION

Various amines are extensively distributed in natural world, and some of which are necessary for keeping life [1, 2]. Polyamines are important in biochemistry because they are present in the cells of microorganisms and animal organisms and contribute to the stabilization of the structure and activity of RNA and DNA [3, 4]. The amine groups have been found to be one of the most efficient functional groups for heavy metal ion removal, and various adsorbents with the amine functional groups have been developed from natural biopolymers [5–7].

The self-assembly and synthesis of metal–organic complexes with supermolecule architectures is now a mature research field [8]. Complexes containing polydentate amine as ligand have been widely discussed in the literature [9–14]. Polydentate amine ligands generally coordinate to transition metal ions using all of the available nitrogen atoms as donors [15]. Transition metal coordination complexes involving tridentate amines as ligands have attracted solid attention for their role as model compounds for bioinorganic systems, as building blocks in supramolecular assemblies and as catalysts [16]. Study of copper(II) complexes is quite interesting because it is biologically active in its chelating ability [17]. Those kinds of complexes possess a wide biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents [18].

As the one of the classics of diamines, 3-oxapentane-1,5-diamine behaves as a tridentate ligand that can form three coordinative bonds with a metal atom through the long pair electrons on two nitrogen atoms and an oxygen atom. In this paper, we have prepared and investigated the spectrum, properties and crystal structure of the two Cu(II) complexes with the ligand of 3-oxapentane-1,5-diamine (Oda)— $[\text{Cu}(\text{Oda})(\text{NO}_3)_2]$ (**I**) and $\{[\text{Cu}(\mu\text{-Oda})(\text{Oda})] \cdot (\text{NO}_3)_2\}_n$ (**II**).

EXPERIMENTAL

Measurements and methods. All chemicals and solvents were reagent grade and used without purification. C, H, and N contents were determined using a Carlo Erba 1106 elemental analyzer. Infrared (IR) spectra were recorded in the range 4000–400 cm^{-1} with a Nicolet FT-IR AVATAR 360 spectrometer using KBr pellets.

Synthesis of Oda was carried out by the procedure given in [19].

For $\text{C}_4\text{H}_{12}\text{N}_2\text{O}$

anal. calcd., %:	C, 46.13;	H, 11.61;	N, 26.90.
Found, %:	C, 45.98;	H, 11.50;	N, 26.76.

IR (KBr; ν , cm^{-1}): 1120, 3340.

Synthesis of I. To a stirred solution of Oda (0.104 g, 1 mmol) in EtOH (10 mL) was added $\text{Cu}(\text{NO}_3)_2 \cdot$

¹ The article is published in the original.

Table 1. Crystallographic data and structure refinement details for complexes **I** and **II**

Parameter	Value	
	I	II
Molecular weight	291.72	395.87
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12^1$
a , Å	8.046(4)	8.4779(8)
b , Å	8.081(4)	13.2607(12)
c , Å	9.419(7)	14.3480(13)
α , deg	104.140(6)	90
β , deg	101.617(6)	90
γ , deg	116.295(4)	90
V , Å ³	497.5(5)	1613.0(3)
Z	2	4
$\rho_{\text{calcd.}}$, g cm ⁻³	1.947	1.630
Absorption coefficient, mm ⁻¹	2.227	1.405
$F(000)$	298	828
Crystal size, mm	0.28 × 0.25 × 0.18	0.38 × 0.30 × 0.27
θ Range for data collection, deg	2.39–24.99	1.42–25.00
Limiting indices hkl	$-9 \leq h \leq 6, -9 \leq k \leq 9, -10 \leq l \leq 11$	$-10 \leq h \leq 10, -15 \leq k \leq 15, -17 \leq l \leq 16$
Refinement collected	2986	11443
Independent reflection (R_{int})	1719 (0.0218)	2842 (0.0508)
Data/restraints/parameters	1719/0/145	2842/0/209
Goodness-of-fit on F^2	1.078	1.044
Final R_1 and wR_2 ($I > 2\sigma(I)$)	0.0301, 0.0751	0.0287, 0.0719
R_1 and wR_2 indices (all data)	0.0337, 0.0772	0.0289, 0.0720
Large diff. peak and hole, $e \text{ \AA}^{-3}$	0.570 and -0.369	0.261 and -0.220

3H₂O (0.242 g, 1 mmol) in EtOH (5 mL). A blue crystalline sediment formed rapidly. The precipitate was filtered off, washed with EtOH and absolute Et₂O, and dried in vacuo. The dried precipitate was dissolved in DMF resulting in a blue solution. The crystals suitable for X-ray diffraction studies were obtained by ether diffusion into DMF after several days at room temperature (the yield was 32% based on the initial Cu(NO₃)₂ · 3H₂O input).

For C₄H₁₂N₄O₇Cu

anal. calcd., %: C, 16.47; H, 4.15; N, 19.21.

Found, %: C, 16.39; H, 4.07; N, 19.15.

IR (KBr; ν , cm⁻¹): 1077, 1379, 3272.

Synthesis of II was carried out by a similar procedure as for complex **I**, the only difference is the amount of the Oda (0.208 g, 2 mmol), which is twice in the process of preparation of complex **I** (the yield was 29% based on the initial Cu(NO₃)₂ · 3H₂O input).

C₈H₂₄N₆O₈Cu

anal. calcd., %: C, 24.27; H, 6.11; N, 21.23.

Found, %: C, 24.46; H, 5.98; N, 21.08.

IR (KBr; ν , cm⁻¹): 1118, 1384; 3251.

Table 2. Selected at distances (Å) and bond and angles (deg) for the complexes **I** and **II***

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
I			
Cu(1)–O(2)	1.973(2)	Cu(1)–N(1)	1.984(3)
Cu(1)–O(1)	2.003(2)	Cu(1)–N(2)	2.007(3)
Cu(1)–O(5)	2.344(2)		
II			
Cu(1)–N(2)	2.006(2)	Cu(1)–N(3)	2.011(2)
Cu(1)–N(1)	2.021(2)	Cu(1)–O(1)	2.080(2)
Cu(1)–N(4) ^{#1}	2.206(2)		
Angle	ω, deg	Angle	ω, deg
I			
O(2)Cu(1)O(1)	171.55(8)	O(2)Cu(1)N(1)	95.10(10)
O(2)Cu(1)N(2)	101.05(10)	N(1)Cu(1)O(1)	87.32(9)
O(1)Cu(1)N(2)	78.86(9)	N(1)Cu(1)N(2)	158.10(11)
N(1)Cu(1)O(5)	88.68(10)	O(2)Cu(1)O(5)	83.52(9)
N(2)Cu(1)O(5)	107.65(11)	O(1)Cu(1)O(5)	88.45(9)
II			
N(2)Cu(1)N(1)	154.32(11)	N(2)Cu(1)N(3)	96.80(10)
N(2)Cu(1)O(1)	81.72(9)	N(3)Cu(1)N(1)	96.51(10)
N(1)Cu(1)O(1)	81.35(9)	N(3)Cu(1)O(1)	169.95(9)
N(3)Cu(1)N(4) ^{#1}	101.14(9)	N(2)Cu(1)N(4) ^{#1}	100.83(10)
O(1)Cu(1)N(4) ^{#1}	88.90(8)	N(1)Cu(1)N(4) ^{#1}	98.01(10)

* Symmetry code for **II**: ^{#1} $-x + 5/2, -y + 1, z - 1/2$.

X-ray crystallography. A suitable single crystal was mounted on a glass fiber and the intensity data were collected on a Bruker Apex-II CCD diffractometer (Bruker AXS Inc., Madison, WI, USA) with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 296(2) K. Data reduction and cell refinement were performed using the SMART and SAINT programs (Bruker AXS Inc., Madison, WI, USA) [20]. The absorption correction was carried out by the empirical method. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL software (Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA) [21]. All hydrogen atoms were found in difference electron maps and were subsequently refined in a riding-model approximation with C–H distances is 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The hydrogen atoms bonded to nitrogen atoms were refined independently

with the distance constraint of N–H = 0.9 Å. Basic crystal data, description of the diffraction experiment, and details of the structure refinement are given in Table 1.

Supplementary material for structures **I**, **II** has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 828193 (**I**) and 828018 (**II**); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSIONS

Two Cu(II) complexes are very stable in the air. They are remarkably soluble in polar aprotic solvents such as DMF, DMSO and MeCN; slightly soluble in ethanol, methanol, ethyl acetate and chloroform; insoluble in water, Et₂O, petroleum ether.

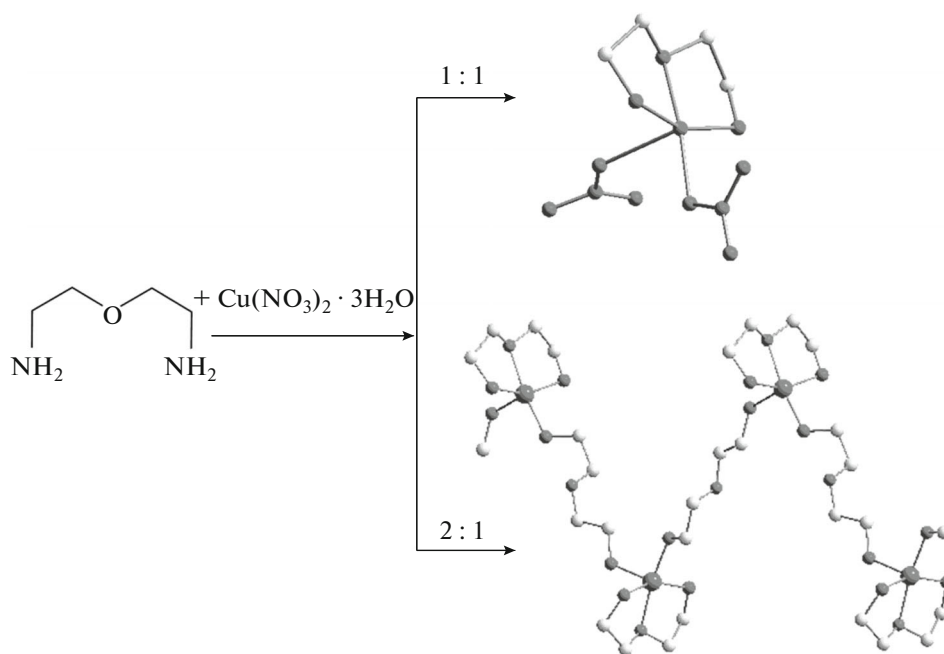


Fig. 1. Series of comparable reactions adjusted by different ratio of ligand Oda and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

Synthetic routine of two Cu(II) complexes is showed in Fig. 1. In our experiments, the different products were obtained by controlling the different molar ratio of Oda and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The Oda and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 1 : 1 ratio form a mononuclear complex, while an infinite 1D chain coordination polymer is obtained in the 2 : 1 ratio. By comparison, the different geometry configuration in two Cu(II) complexes suggested that the excess of Oda may be as bridge ligand in coordination polymer.

The IR spectra of the complexes show that the strong absorption $\nu(\text{NH}_2)$ and $\nu(\text{C}-\text{O}-\text{C})$, which appear at 3340 and 1120 cm^{-1} in the free ligands Oda, is shifted to lower wave numbers, corresponding bands appear 3272, 1077 cm^{-1} in complex I and 3251, 1118 cm^{-1} in complex II, respectively, which indicate that the nitrogen and oxygen atoms of the ligand are coordinated to the Cu(II) atom in two complexes. The band at 1379 cm^{-1} in complex I and 1384 cm^{-1} in complex II are attributed to $\nu(\text{NO}_3^-)$.

Selected bond distances and angles of I are presented in Table 2. The ORTEP structure (30% probability ellipsoids) of complex I with atom labeling is shown in Fig. 2a. The molecular structure consists of a Oda, two nitrate radical, and one Cu(II) atom. The Cu(II) in the complex is N,O,N'-chelated by Oda and is further coordinated by two nitrate anions. The coordination geometry of the Cu(II) atom may be best described as distorted square-base pyramidal ($\tau = 0.22$). The τ parameter is defined as $(\beta - \alpha)/60$ (where $\beta =$

$\text{O}(2)\text{Cu}(1)\text{O}(1)$, $\alpha = \text{N}(1)\text{Cu}(1)\text{N}(2)$) and its value varies from 0 (in regular square-base pyramidal) to 1 (in regular trigonal-bipyramidal) [22, 23]. The equatorial plane is occupied by N_2O of ligand Oda, and one O atom of nitrate radical, whereas the Cu(II) atom protrudes towards O(5) by 0.063 Å from the plane of atoms N(1)/N(2)/O(1)/O(2).

Selected hydrogen bonds are listed in Table 3. N—H···O hydrogen-bonding interactions play important roles in the crystal packing modes in the complex I (Fig. 3a). The introductions of NH_2 groups in the frameworks successfully lead to the assembly of these monomeric units by intermolecular hydrogen bonds. As illustrated in Fig. 3, intermolecular N—H···O hydrogen bonds interlink the units through the nitrate radical into a 1D network.

Selected bond distances and angles of II are presented in Table 2. The ORTEP structure (30% probability ellipsoids) of complex II with atom labeling is shown in Fig. 2b. The unit of polymer is characterized by $\{[\text{Cu}(\text{Oda})_2] \cdot (\text{NO}_3)_2\}_n$ units linked into polymeric chains, where one Oda connects the adjacent Cu(II) atoms of the symmetry related unit in an end-to-end bridging mode (Fig. 4). The Cu(II) atom in the complex is N,O,N'-chelated by Oda and is further coordinated by two nitrogen from two bridging Oda. The coordination geometry of the Cu(II) atom may be best described as distorted square-base pyramidal ($\tau = 0.26$). The equatorial plane is occupied by N_2O of ligand and one N atom of bridging Oda, whereas the

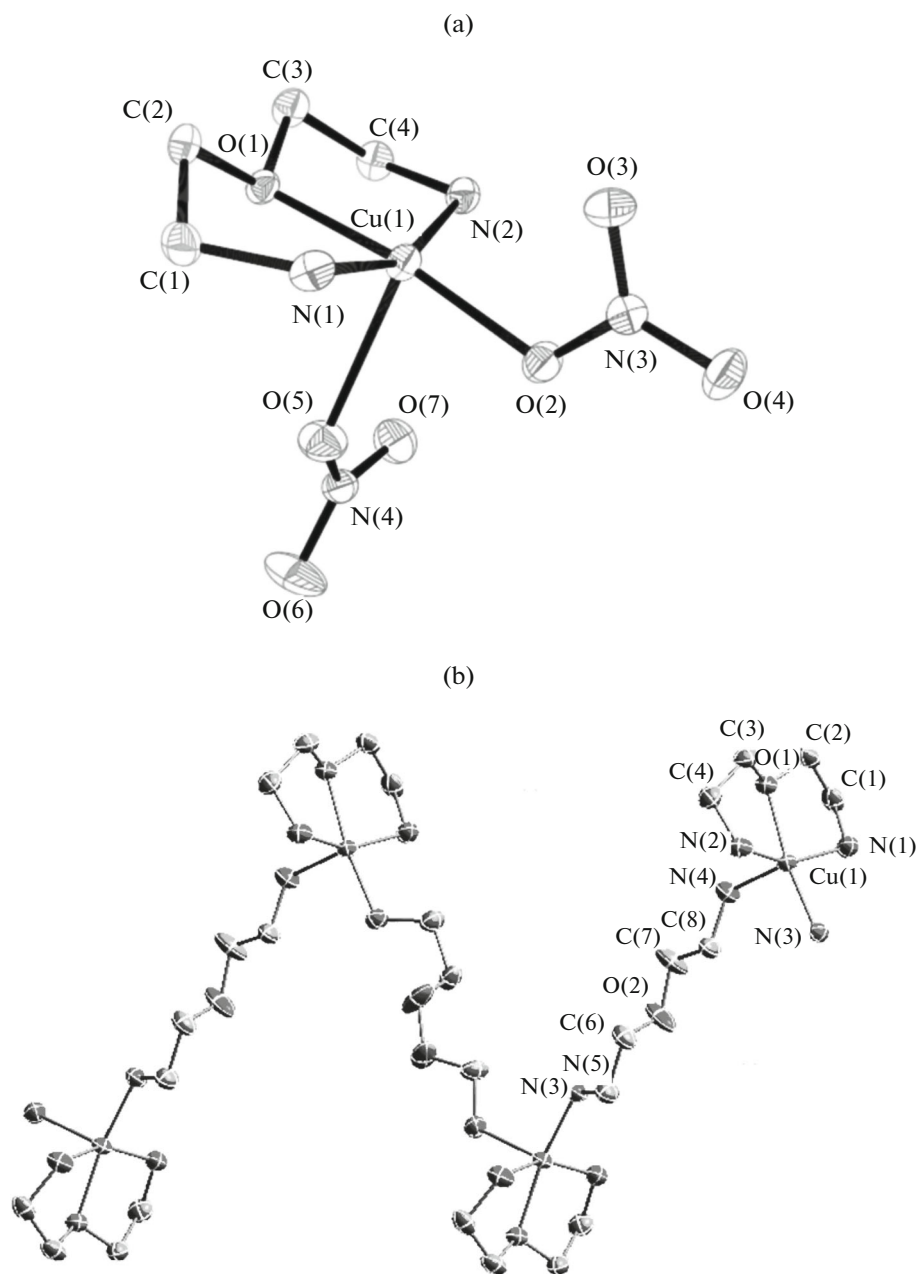


Fig. 2. Molecular structure of complexes I (a) and II (b) and atom numberings of I with hydrogen atoms omitted for clarity.

Cu(II) atom protrudes towards O(5) by 0.268 Å from the plane of atoms N(1)/N(2)/N(3)/O(1). The Cu–N (equatorial) bond distance in complex II ranging between 2.006(2) and 2.080(2) Å (Table 2) are consistent with the corresponding reported values for analogous Cu(II) systems [24, 25]. The shortening of the Cu–N equatorial bond lengths in comparison to the Cu–N (axial) lengths (2.206 Å) is a result of the Jahn–Teller effect for the d^9 configuration of the Cu(II) atom in a pentagonal environment [26]. Intermolecu-

lar N–H \cdots O hydrogen bonds, interlink the chains through the nitrate radical into a two-dimensional network (Fig. 3b). The selected hydrogen bonds are listed in Table 3.

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Table 3. Geometric parameters hydrogen bonds of complexes **I** and **II**

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
N(2)–H(2B)···O(2) ^{#1}	0.90	2.35	3.120(4)	144
N(2)–H(2A)···O(6) ^{#2}	0.90	2.28	3.050(4)	143
C(1)–H(1C)···O(6) ^{#3}	0.97	2.60	3.373(5)	137
N(1)–H(1B)···O(7) ^{#3}	0.90	2.54	3.351(4)	150
N(1)–H(1A)···O(5) ^{#4}	0.90	2.45	3.192(4)	140
N(1)–H(1A)···O(2) ^{#4}	0.90	2.53	3.312(4)	145
II				
C(4)–H(1B)···O(7) ^{#4}	0.97	2.60	3.526(4)	160
C(5)–H(5D)···O(7) ^{#5}	0.97	2.32	3.175(4)	147
N(1)–H(11A)···O(7) ^{#5}	0.90	2.17	3.041(3)	162
N(2)–H(10B)···O(5) ^{#2}	0.90	2.34	3.107(4)	143
N(2)–H(10B)···O(3) ^{#2}	0.90	2.36	3.199(3)	156
N(4)–H(5A)···O(7) ^{#6}	0.90	2.16	3.030(3)	163
N(1)–H(11B)···O(8) ^{#7}	0.90	2.25	3.020(4)	143
N(3)–H(7B)···O(6) ^{#7}	0.90	2.11	2.985(4)	164
N(4)–H(5B)···O(4) ^{#7}	0.90	2.47	3.290(4)	152
N(4)–H(5B)···O(3) ^{#7}	0.90	2.39	3.217(3)	152
N(3)–H(7A)···O(5) ^{#8}	0.90	2.16	3.049(3)	172
N(2)–H(10A)···O(5) ^{#8}	0.90	2.52	3.122(4)	124
N(2)–H(10A)···O(4) ^{#8}	0.90	2.27	3.170(4)	177
N(3)–H(7A)···O(5) ^{#8}	0.90	2.16	3.049(3)	172
C(8)–H(8B)···O(6) ^{#9}	0.97	2.31	3.241(4)	160

Symmetry codes: for **I** ^{#1} $-x, -y + 1, -z + 1$; ^{#2} $x, y - 1, z$; ^{#3} $x + 1, y, z$; ^{#4} $-x + 1, -y + 2, -z + 1$ and for **II** ^{#1} $-x + 5/2, -y + 1, z - 1/2$; ^{#2} x, y, z ; ^{#3} $-x + 5/2, -y + 1, z + 1/2$; ^{#4} $-x + 1, y - 1/2, -z + 1/2$; ^{#5} $x + 1/2, -y + 3/2, -z + 1$; ^{#6} $x + 3/2, -y + 3/2, -z + 1$; ^{#7} $x + 1, y, z$; ^{#8} $x + 1/2, -y + 1/2, -z + 1$; ^{#9} $-x + 3/2, -y + 1, z + 1/2$.

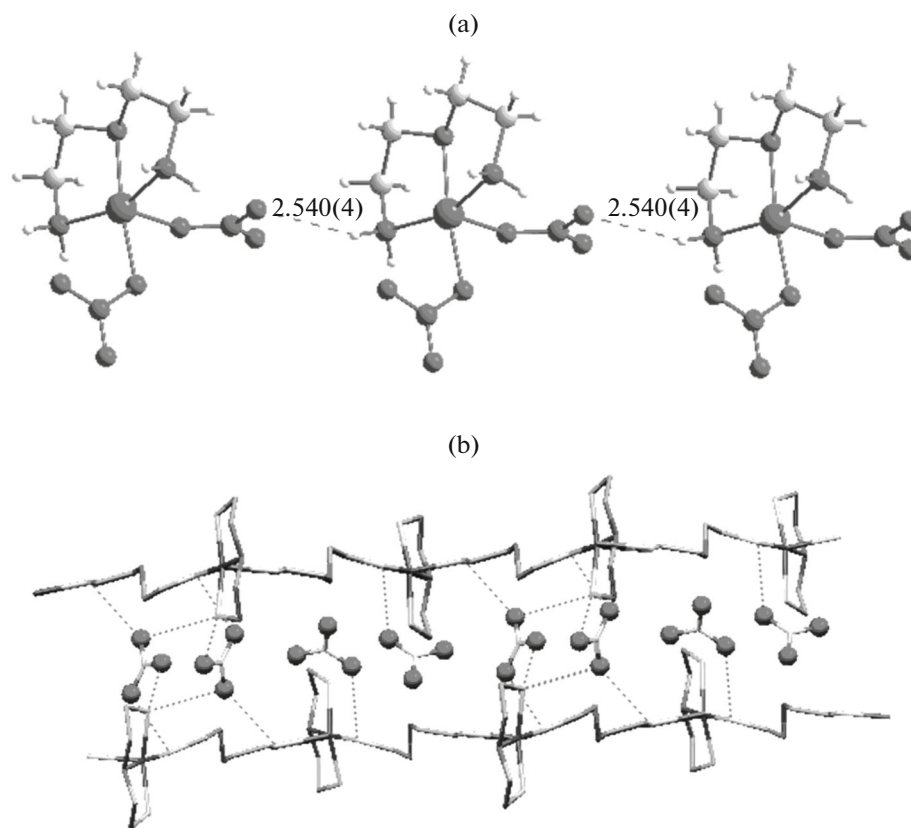


Fig. 3. View of N–H···O hydrogen bonds interaction in complexes I (a) and II (b).

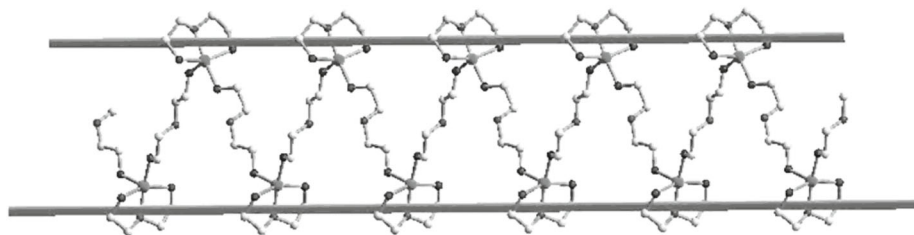


Fig. 4. Diagram showing stacking of 1D chain of complex II.

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