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Cadmium(II) and Nickel(II) 1-Oxypyridyl-2-Selenolates: Synthesis and Molecular and Crystal Structures

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Abstract—Cadmium ($C_{20}H_{16}Cd_2N_4O_4Se_4$) (**I**) and nickel ($C_{10}H_8N_2NiO_2Se_2$) (**II**) selenolates are synthesized by the exchange reactions of sodium 1-oxypyridyl-2-selenolate and cadmium(II) and nickel(II) chlorides. The molecular and crystal structures of the complexes are determined by X-ray structure analysis (CIF files CCDC nos. 1585246 (**I**) and 1585251 (**II**)). Complex **I** forms a centrosymmetric dimer in which the coordination polyhedron of the cadmium atom is a distorted trigonal bipyramid and the selenium atoms take the *trans* configuration. Complex **II** containing the solvate C_2H_5OH molecule has a square structure and is a monomer. Unlike complex **I**, in complex **II** the selenium atoms of the ligands take the *cis* configuration. The crystal packings in complexes **I** and **II** are formed by weak intermolecular hydrogen bonds C–H···O and C–H···Se.

Keywords: 2-selenopyridine-1-oxide, crystal packing, X-ray structure analysis

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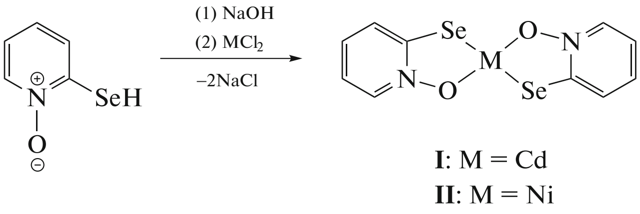
INTRODUCTION

It is known that complexes based on 2-mercaptopyridine-1-oxide, such as zinc and copper pyrithiones, are characterized by a broad range of biological activity and find commercial use as industrial fungicides and biocides in cutting fluids and manufacturing of paintwork materials and makeup preparations [1–5]. Increased interest has been given in the recent years to studying organoselenium compounds due to their high synthetic potential and practical value [5, 6]. In particular, it is found that the selenium-containing analog of zinc pyridinethione, bis(2-selenopyridine-1-oxide)zinc(II), and the corresponding nickel, copper, and cadmium salts are characterized by significant fungicidal and bactericidal activity [7–11]. The syntheses and X-ray structure analysis data for bis(2-selenopyridine-1-oxide)zinc(II) and bis(2-selenopyridine-1-oxide)nickel(II) solvate with acetone were described earlier [12, 13].

In this work, we present the results of X-ray structure analyses of new complexes based on 2-selenopyridine-1-oxide (HL): bis(2-selenopyridine-1-oxide)cadmium(II) ($C_{20}H_{16}Cd_2N_4O_4Se_4$) (**I**) and nickel(II) (solvate) ($C_{10}H_8N_2NiO_2Se_2$) (**II** · $0.5C_2H_5OH$).

Complexes **I** and **II** were synthesized via the following scheme:



I: M = Cd
II: M = Ni

EXPERIMENTAL

Synthesis of complex I. A solution of NaOH (0.08 g, 2 mmol) in water (5 mL) and a solution of $CdCl_2$ (0.183 g, 1 mmol) in water (10 mL) were added to a solution of HL (0.348 g, 2 mmol) in ethanol (5 mL) at room temperature. A white precipitate that formed in 10 min was filtered off. The product was washed with water, ethanol, and diethyl ether and dried in air. The yield was 0.43 g (94%), mp = 263–265°C. Colorless crystals of compound **I** suitable for X-ray structure analysis were obtained by the slow crystallization of a solution of the compound in ethanol at room temperature.

For $C_{20}H_{16}N_4O_4Se_4Cd_2$

Anal. calcd., %	C, 26.19	H, 1.76	N, 6.11
Found, %	C, 26.09	H, 1.72	N, 6.05

Synthesis of complex II. A solution of NaOH (0.08 g, 2 mmol) in water (5 mL) and a solution of $NiCl_2$ (0.129 g, 1 mmol) in water (10 mL) were added to a solution of HL (0.348 g, 2 mmol) in ethanol (5 mL) at room temperature. A brown precipitate that formed in 10 min was filtered off. The product was washed with water, ethanol, and diethyl ether and dried in air. The yield was 0.39 g (91%), mp = 282–283°C. Green crystals of compound **II** used for X-ray structure analysis were obtained by the slow crystallization of a solution of the compound in ethanol at room temperature.

For $C_{11}H_{11}N_2O_{2.5}Se_2Ni$

Anal. calcd., %	C, 30.88	H, 2.59	N, 6.55
Found, %	C, 30.79	H, 2.51	N, 6.47

X-ray structure analysis. The crystallographic data for compounds **I** and **II** were obtained on a Bruker Smart Apex diffractometer (ω scan mode, MoK_α radiation, $\lambda = 0.71073$ Å, $T = 100$ and 296 K). Experimental sets of reflection intensities were collected and integrated using the SMART [14] and SAINT [15] programs, respectively. The structures were solved by a direct method and refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms. The hydrogen atom of the solvate molecule involved in the formation of the intermolecular hydrogen bond O(3)–H(3)···O(1) in compound **II** was localized from the difference electron density synthesis and refined in the isotropic approximation. Other hydrogen atoms in compounds **I** and **II** were placed in the geometrically calculated positions and refined isotropically with the fixed thermal parameters $U_{\rm iso}(H) = 1.2U_{\rm iso}(C)$. The structures were refined and absorption corrections were applied using the SHELXTL [16] and SADABS [17] program packages. The crystallographic data and parameters of X-ray structure experiments are presented in Table 1.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1585246 (**I**) and 1585251 (**II**); http://ccdc.cam.ac.uk/getstructures).

RESULTS AND DISCUSSION

Compounds **I** and **II** represent two basically different structural types. Complex **I** is a centrosymmetric dimer $[M_2(SeOPy)_4]$ (Fig. 1a). The coordination polyhedron of the cadmium(II) atom in complex **I** is a distorted trigonal bipyramid with the Se(1), Se(2), and O(2*A*) atoms in the equatorial plane, the O(1) and O(2) atoms in the axial positions, and the O(1)Cd(1)O(2) angle equal to 167.2(1)°. A molecule of compound **I** has intrinsic symmetry C_2, and the 2-fold axis passes through the center of a rhombus consisting of the O(2), O(2*A*), Cd(1), and Cd(1*A*) atoms. The Cd(1)–Cd(1*A*) distance in dimeric complex **I** is 3.680(4) Å, the Cd–O distance is 2.269(3)–2.383(3) Å, the average Cd···O distance is 2.341(3) Å, and the deviation of individual values from an average value does not exceed 3σ. The Cd–Se(1,2) distances are 2.559(5) and 2.563(5) Å, respectively. The Se(1)–C(1,6) and Se(2)–C(6) bond lengths (1.879(4) and 1.871 Å, respectively) are comparable with the sum of covalent radii of Se and C atoms (1.95 Å) [18]. The dihedral angle between the plane of the Cd(1)–Se(1)–C(1)–N(1)–O(1) and Cd(1)–Se(2)–C(6)–N(2)–O(2) cycles is 32.0(8)°. The selenium atoms of two ligands in complex **I** take the *trans* configuration.

In crystal the dimers of compound **I** form piles along the *a* crystallographic axis. Intermolecular hydrogen bonds Se···H and O···H are observed between the adjacent molecules of complex **I** along the direction of the *a* axis. The Se(2)···H(4*A*) and Se(2)···H(5*A*) distances ($-x + 2, y + 1/2, -z + 3/2$) are 3.01 and 3.04 Å, respectively, which is somewhat less than the sum of the van der Waals radii of Se and H atoms (3.15 Å) [17]. The O(2)···H(9*A*) distance ($-x + 1, y - 1/2, -z + 1/2$) equal to 2.43 Å lies in a range of 2.15–2.45 Å between the average van der Waals contact and specific (shortened) O···H interaction [19] (Fig. 2).

In addition, a short intermolecular contact C(3)···C(10) is observed between the adjacent molecules along the *a* axis. The C···C distance (3.309(6) Å) corresponds to the weak secondary interaction C···C (between 3.27 and 3.42 Å [19]).

Selected bond lengths and bond angles in compound **I** are presented in Table 2.

The monomer of compound **II** has the composition $[M(SeOPy)_2]$ and contains the solvate molecule C_2H_5OH (in a ratio of 1 : 0.5) (Fig. 1b). The nickel atom has a distorted square coordination mode by the Se(1) and Se(2) selenium atoms and the O(1) and O(2) atoms of two ligands. The average deviation from the square plane of four atoms coordinated to the nickel(II) atom is 0.038 Å. The ONiO (85.4(1)°) and SeNiSe (94.61(3)°) angles characterize the deviations from the ideal square arrangement of the donor atoms. A molecule of complex **II** is nearly planar: the average deviations of all atoms from the root-mean-square plane are 0.039 Å. The Ni(1)–O(1,2) and Ni(1)–Se(1,2) bond lengths (1.863(3), 1.875(3) and 2.2473(7), 2.2495(7) Å, respectively) are close to similar distances in the isostructural nickel complex [12]. The Se(1)–C(1) and Se(2)–C(6) distances in complex **II** (1.894(5) and 1.888(4) Å) are comparable with

Table 1. Main crystallographic data and refinement parameters for compounds **I** and **II**

Parameters	Value	
	I	**II**
FW	917.01	427.85
Crystal sizes, mm	0.620 × 0.340 × 0.210	0.150 × 0.090 × 0.060
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a, Å	8.3134(5)	16.4116(11)
b, Å	10.3852(6)	7.7854(5)
c, Å	13.8060(8)	21.8567(15)
β, deg	94.2860(10)	92.4954(11)
V, Å^3	1188.63(12)	2790.0(3)
Z	2	8
ρ_{calcd}, g/cm^3	2.562	2.037
μ, mm^{-1}	7.950	6.608
$F(000)$	856	1656
T_{min}; T_{max}	0.0073; 0.0524	0.7457; 0.3398
Data collection range over θ, deg	2.5–33.0	1.9–28.0
Measured reflections	18447	13949
Independent reflections	4510	3446
Number of reflected parameters	154	181
GOOF	1.072	1.007
R_1 ($I > 2\sigma(I)$)	0.0486	0.0518
wR_2 (all data)	0.1432	0.1128
Residual electron density ($\Delta\rho_{min}/\Delta\rho_{max}$), e Å^{-3}	–2.059/2.975	–1.224/1.457

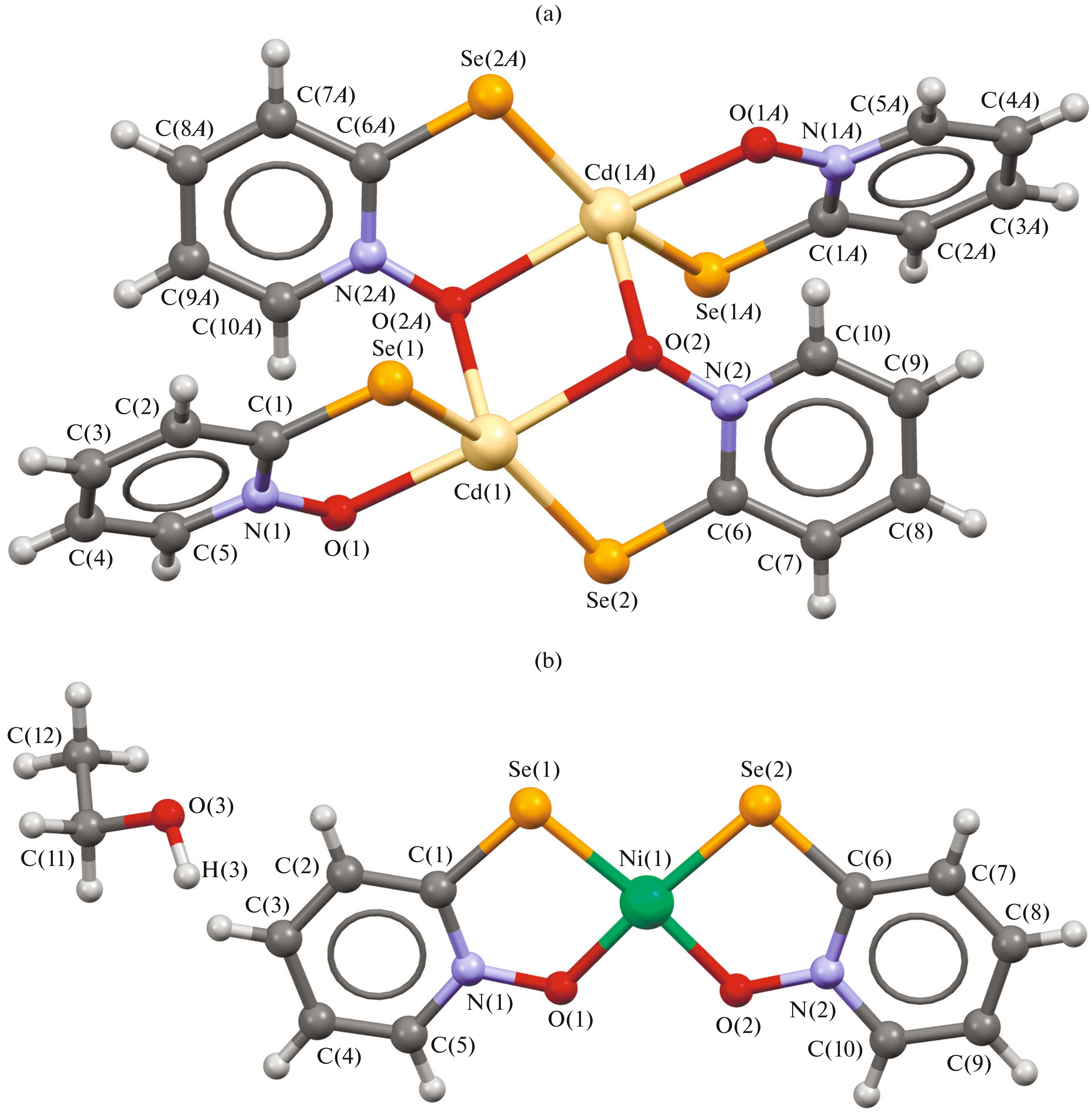


Fig. 1. Molecular structures of compounds (a) **I** and (b) **II**.

the sum of covalent radii of Se and C atoms (1.95 Å) [18]. The dihedral angle between the Ni(1)–O(1)–Se(1)–N(1)–C(1) and Ni(1)–O(2)–Se(2)–N(6)–C(6) planes is 3.54(9)°.

Unlike complex **I**, in compound **II** the selenium atoms of the ligands take the *cis* configuration.

In crystal the planar molecules of compound **II** form pairwise linked dimers due to weak contacts O···H–C (O(2)···H(10*A*) (–*x*, *y*, –*z* + 1/2)) (C–H 0.93, H···O 2.40 Å, angle C–H···O 162°) (Fig. 3a).

Additional hydrogen bonds Se···H and O···H with the distances at a level of shortened and van der Waals interactions are observed in the crystal of complex **II** along with the listed above intermolecular contacts. The Se(2)···H(5*A*) (*x* – 1/2, *y* – 1/2, *z*) and (Se(1)···H(9*A*) (*x*, –*y* + 2, *z* – 1/2)) distances (2.92 and 3.13 Å, respectively) are less than the sum of the van der Waals radii of Se and H atoms (3.15 Å) [17] (Fig. 3b). The O···H distances between the solvate molecule of ethanol and the molecule of complex **II** (O(1)···H(3*A*) (–*x*, –*y* + 1, –*z* + 1)) and (O(3)···H(7*A*)

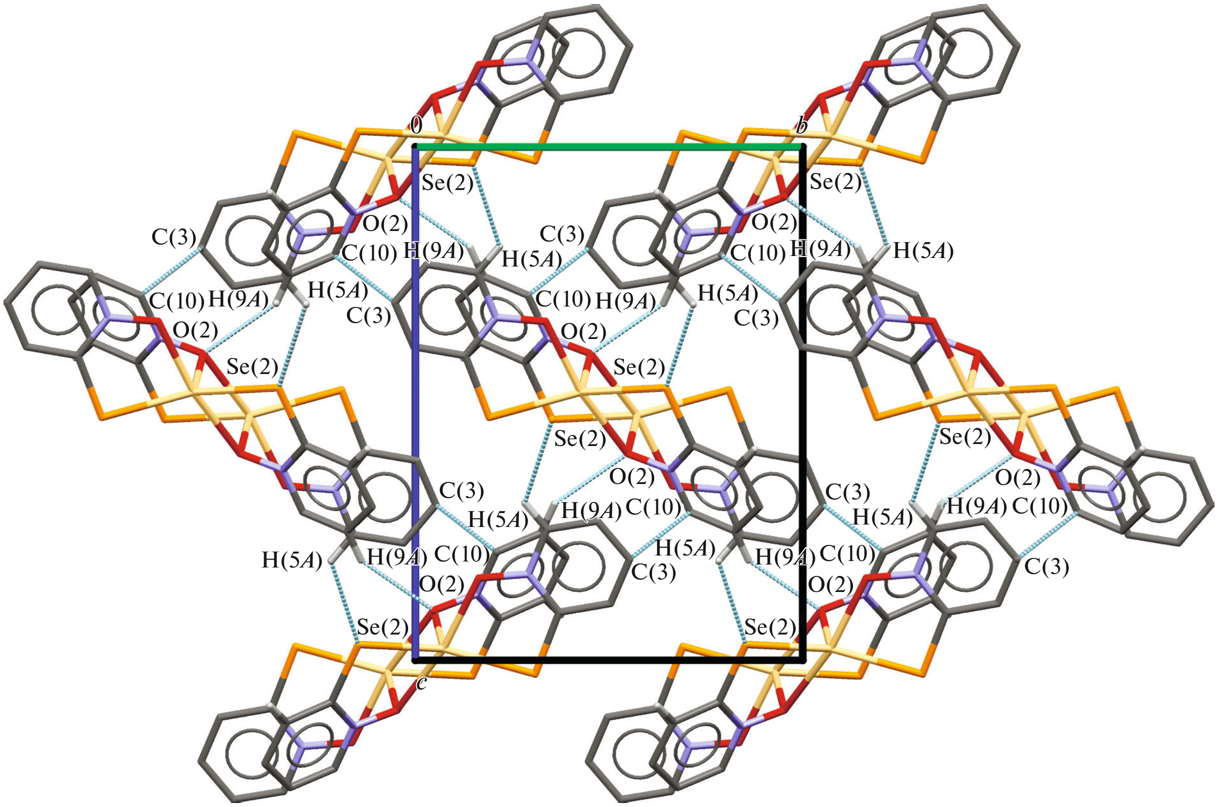


Fig. 2. Fragment of the crystal packing of compound **I** in the projection onto the *b*0*c* plane. Contacts Se···H, O···H, and C···C are shown by dash. Hydrogen atoms that are not involved in intermolecular hydrogen contacts are omitted for clarity.

Table 2. Selective bond lengths and bond angles in compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Cd(1)–O(1)	2.269(3)	Se(1)–C(1)	1.879(4)
Cd(1)–O(2)	2.373(3)	Se(2)–C(6)	1.872(4)
Cd(1)–O(2*A*)	2.383(3)	O(1)–N(1)	1.333(4)
Cd(1)–Se(1)	2.5586(5)	O(2)–N(2)	1.343(4)
Cd(1)–Se(2)	2.5629(5)		
	II		
Ni(1)–O(1)	1.863(3)	Se(2)–C(6)	1.887(5)
Ni(1)–O(2)	1.875(3)	O(1)–N(1)	1.359(4)
Ni(1)–Se(2)	2.2473(7)	O(2)–N(2)	1.346(5)
Ni(1)–Se(1)	2.2495(7)	O(3)–C(11)	1.426(3)
Se(1)–C(1)	2.5629(5)	C(11)–C(12)	1.503(3)
Angle	ω, deg	Angle	ω, deg
	I		
O(2*A*)Cd(1)Se(1)	98.56(7)	O(1)Cd(1)O(2)	167.17(11)
O(1)Cd(1)Se(2)	99.96(7)	O(1)Cd(1)O(2*A*)	90.23(11)
O(2)Cd(1)Se(2)	77.65(7)	O(2)Cd(1)O(2*A*)	78.58(10)
O(2*A*)Cd(1)Se(2)	106.85(7)	O(1)Cd(1)Se(1)	81.26(7)
Se(1)Cd(1)Se(2)	154.536(17)	O(2)Cd(1)Se(1)	106.41(7)
Cd(1)O(2)Cd(1*A*)	101.42(10)		
	II		
O(1)Ni(1)O(2)	85.36(13)	Se(2)Ni(1)Se(1)	94.61(2)
O(1)Ni(1)Se(2)	175.07(9)	C(1)Se(1)Ni(1)	92.85(12)
O(2)Ni(1)Se(2)	89.91(10)	C(6)Se(2)Ni(1)	93.21(13)
O(1)Ni(1)Se(1)	90.19(9)	N(1)O(1)Ni(1)	119.5(2)
O(2)Ni(1)Se(1)	174.58(10)	N(2)O(2)Ni(1)	119.4(2)

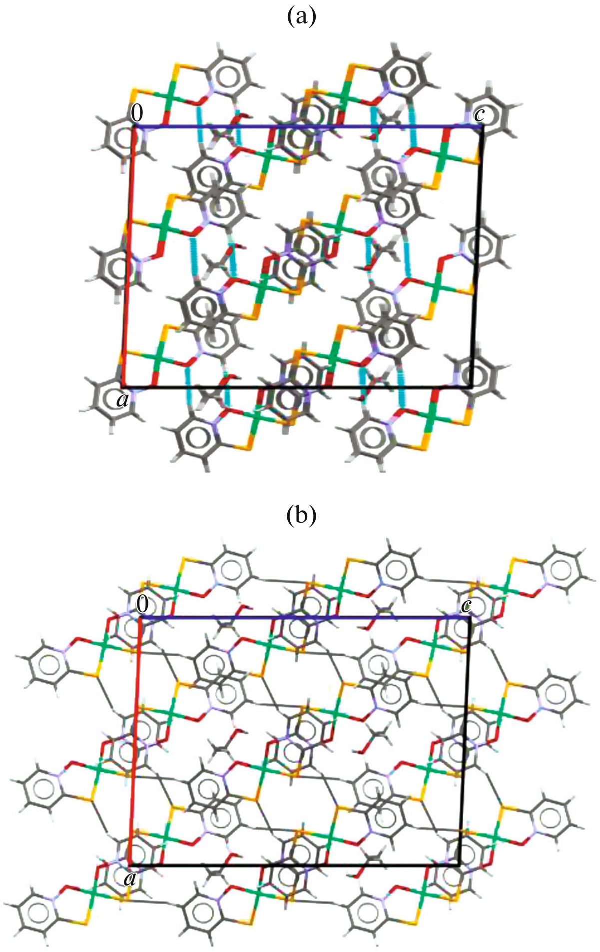


Fig. 3. Fragment of the crystal packing of compound **II** in the projection onto the $a0c$ plane. Contacts (a) O···H and (b) Se···H are shown by dash.

($-x + 1/2$, $-y + 3/2$, $-z + 1$)) are 2.15 and 2.42 Å, respectively, and lie in a range of 2.15–2.45 Å between the specific (shortened) contact and the average van der Waals O···H interaction [19].

Selected bond lengths and bond angles in compound **II** are presented in Table 2.

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